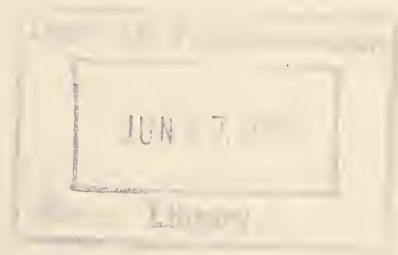L 1975

INTRODUCTION TO

CONCRETE-POLYMER MATERIALS

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16. Abstract

The purpose of this text is to provide highway personnel with a working knowledge of concrete polymer development and application. Basic information necessary to begin experimental application of these materials is presented.

The text presents discussions on the following: (1) a review of concrete-polymer materials development, (2) knowledge of polymer chemistry as applied to concrete-polymer materials, (3) knowledge of the technology required to produce concrete-polymer materials, (4) a description of the fundamental characteristics and properties of the composites, and (5) an in-depth study of the applications of concrete-polymer materials.

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PREFACE

At the request of the Implementation Division of the Federal Highway Administration, an introductory course on Concrete-Polymer Materials was given by the staff of Brookhaven National Laboratory. The purpose of the course was to provide representatives of State Highway Departments with a working knowledge of concrete-polymer materials development and applications.

The course, which was presented in a one-week series of lectures and laboratory demonstrations, was designed to provide the following information: (1) a review of concrete-polymer materials development, (2) knowledge of polymer chemistry as applied to concrete-polymer materials, (3) knowledge of the technology required to produce concrete-polymer materials, (4) a description of the fundamental characteristics and properties of the composites, and (5) an in-depth study of the applications of concrete-polymer materials.

It is hoped that this course and the following text will enable other workers to commence studies that could lead to the use of concrete-polymer materials in solving some of the immense problems confronting the highway industry today.

CONTENTS

CONCRETE-POLYMER MATERIALS

Classification and Terminology

Three general types of concrete material to which polymer is added to form composite materials are classified as concrete-polymer materials.

1. <u>Polymer-impregnated concrete</u> (PIC) is a precast portland cement concrete impregnated with a monomer, which is subsequently polymerized <u>in situ</u>.

2. <u>Polymer concrete</u> (PC) is a composite material formed by polymerizing a monomer and aggregate mixture. The polymerized monomer acts as the binder for the aggregate.

3. <u>Polymer cement concrete</u> (PCC) or <u>polymer portland cement concrete</u> (PPCC) is a premixed material: a monomer or polymer in the form of a latex is added to a fresh concrete mix and subsequently cured and polymerized in place.

Monomers and polymers are incorporated in these materials for the purpose of substantially altering some property of the final hardened concrete material. Small quantities of polymer are sometimes added to modify the properties of fresh concrete; such materials are more appropriately considered to be admixtures and are not considered in this text.

It is recognized in the above classification that the general definition of a <u>concrete</u> is an aggregate bound with a binder. In ordinary concrete, portland cement usually acts as a binder. In PIC the polymer acts together with the cement binder, and in PC the polymer alone acts as the binder.

The definition of a <u>monomer</u> is an organic molecular species that is capable of combining chemically with molecules of the same species or with other species to form a polymeric material of higher molecular weight.

A <u>polymer</u> is defined as an organic material composed of a series of repeating chemical units (the unit being defined as a monomer) that are linked together chemically.

CHAPTER I
HISTORICAL REVIEW OF CONCRETE-POLYMER MATERIALS DEVELOPMENT
M. Steinberg

After seven years of research and development work, concrete-polymer materials are beginning to emerge from the laboratory into the field as a material of construction with worldwide potential.

The first sample of polymer-impregnated concrete (PIC) was produced at Brookhaven National Laboratory (BNL) in the fall of 1965. Since 1967, under the auspices and with the support of the U.S. Atomic Energy Commission's Division of Isotopes Development (later absorbed into the Division of Applied Technology), and in cooperation with the Bureau of Reclamation (USBR), BNL has developed the monomer-material formulations and the methods of impregnation, measured the structural and durability properties, and initiated development of practical applications. The basic patent on polymer-impregnated concrete (PIC) was obtained by BNL and is assigned to the U.S. Atomic Energy Commission (U.S. Patent 3,567,496, March 2, 1971). Initially the material was produced by radiation polymerization. However, the thermal-chemical means of initiation is more economical and readily applied, and the patent covers the thermal-chemical process.

The results of this work are summarized in a number of publications, notably, five topical reports [1-5] that review in detail the information gained and progress made in this work. Lectures and papers on concrete-polymers have been presented at local and national scientific, engineering, and trade societies, including the American Concrete Institute, the American Chemical Society, the American Ceramic Society, the American Nuclear Society, and the Transportation Research Board of the National Academy of Sciences.

PIC, basically a concrete material, is of interest because of its greatly improved structural and durability properties compared with those of ordinary concrete. PIC has attracted the attention of concrete workers and companies around the world, and much development for applications has been initiated both nationally and internationally.

In the U.S., the Federal Highway Administration (FHWA) has instituted programs at BNL and the USBR on construction of new precast bridge decks for highway applications. The FHWA and the Transportation Research Board (TRB) have instituted programs in universities and at the USBR and BNL on impregnation of cast-in-place new and old concrete for the purpose of, first, preventing deterioration of recently placed concrete, and second, repairing concrete that has already deteriorated on older bridge decks. The Office of Saline Water (OSW) has supported work at BNL and USBR to develop chemically resistant PIC for operation at elevated

temperatures in multistage distillation vessels in large sea-
water desalting plants. The Bureau of Mines has supported work
at BNL on improving the structural stability of roof and wall
structures in mines. The American Concrete Pipe Association
has initiated work on PIC pipe for the purpose of producing
a stronger and more durable pipe and thus eliminating the need
for costly steel reinforcing. The Department of the Interior
has supported work at the USBR on producing and testing PIC for
tunnel linings for water carriers. The interest in other items
such as building block, railroad ties, beams, and ferrocement
boats continues unabated.

In foreign countries, interest has been high and applica-
tions have been numerous. The Japanese have built a pilot plant
and have produced and used PIC for furniture, base plates for
pumps in corrosive chemical plants, electric cable covers, heated
road panels, and underwater structures. The Norwegians have in-
stalled PIC curbing on streets in Oslo. The South Africans have
made PIC mirror concrete for bathroom and kitchen basins, tile,
and PIC pipe. The Soviet Union is developing a number of different
forms of polymer-concrete and is beginning to use PIC decorative
panels for building facades in Moscow. An Italian cement company
near Rome has instituted an extensive concrete-polymer program
and is using the material in a structural decorative panel for a
high-rise building. England, France, Spain, and Israel also have
independent programs on concrete-polymers. The American Concrete
Institute (ACI) has established a committee (ACI-548, Polymers
in Concrete) and two symposia have already been held. A state-
of-the-art report on concrete-polymer will be issued shortly.
Considering that concrete is one of the oldest materials of
construction, known for thousands of years, the interest in the
development of PIC and its growth is truly remarkable.

Research on concrete-polymer materials has been expanded to
include lightweight aggregate PIC, the development of polymer
concrete, and the incorporation of urban solid waste in PIC
and PC. Glass-polymer composite (GPC) materials are an example
of the latter; nonreturnable glass bottles or glass-containing
incinerator ash is used as an aggregate and is mixed with monomer
to produce a strong, corrosion-resistant sewer pipe.

A paper polymer composite (PPC) containing wastepaper or
newsprint has also been developed. This strong, durable, boardlike
material is suitable for wall board, pallets, and traffic signs.
These recycled solid waste materials are of great interest to
environmental groups and governmental agencies as a potential
means of solving part of the country's solid waste disposal
problem.

Stone has also been impregnated with polymer. This material
has been shown to be of value in mine roof support systems and
in the preservation of modern and ancient art work and monuments.

REVIEW OF CONCRETE-POLYMER MATERIALS:
THEIR PREPARATION, PROPERTIES AND APPLICATION
M. Steinberg

Introduction

The concrete-polymer composite materials development program
is directed toward developing both improved and new concrete
materials by combining the ancient technology of hydraulic
cement concrete formation with the more modern technology of
polymer chemistry. A wide range of concrete-polymer composites
have been investigated.

Polymer-Impregnated Concrete Materials Development

Polymer-impregnated concrete (PIC) is a precast and cured
hydrated cement concrete that has been impregnated with a low
viscosity monomer and polymerized in situ. This material is
the most developed of the composites. The greatest improvements
in structural and durability properties have been obtained with
PIC. With normal-weight concrete, compressive strengths can be
increased from 5000 to 20,000 psi. Water absorption is reduced
by 99%, and the freeze-thaw resistance is enormously improved.
With high-silica cement, strong basaltic aggregate, and high-
temperature steam curing, strength increases from 12,000 to
over 38,000 psi can be obtained. The tensile strength of PIC
is about ten times less than the compressive strength, as in
conventional concrete. A maximum tensile strength of 3500 psi
has been obtained with the steam-cured concrete. With fog-
cured concrete, polymer loadings (e.g.) polymethyl methacrylate,
(PMMA), of about 6% by weight (wt polymer/wt of dried concrete)
are obtained. A freeze-thaw test specimen of PIC is shown in
Figure 2-1, and a sample exposed to chemical attack by acids
is shown in Figure 2-2.

After impregnation, conventional concrete is transformed
from a plastic material to an essentially elastic material,
as indicated by the linearity of the stress-strain plot for PIC
in Figure 2-3. The modulus of elasticity is increased by at
least a factor of 2. The ability to vary the shape of the
stress-strain curve presents some interesing possibilties for
tailoring desired properties of concrete to particular structural
applications. This may be achieved by adding plasticizers to
the monomer systems or varying the type and shape of aggregate,
e.g., steel fiber aggregate.

In contrast to conventional concrete, PIC exhibits essen-
tially zero creep properties, as shown graphically in Figure 2-4.

Figure 2-1. Freeze-thaw test on polymer-impregnated concrete. PIC contains 6 wt. % PMMA and lost 0.5% weight. Control lost 26.5%.
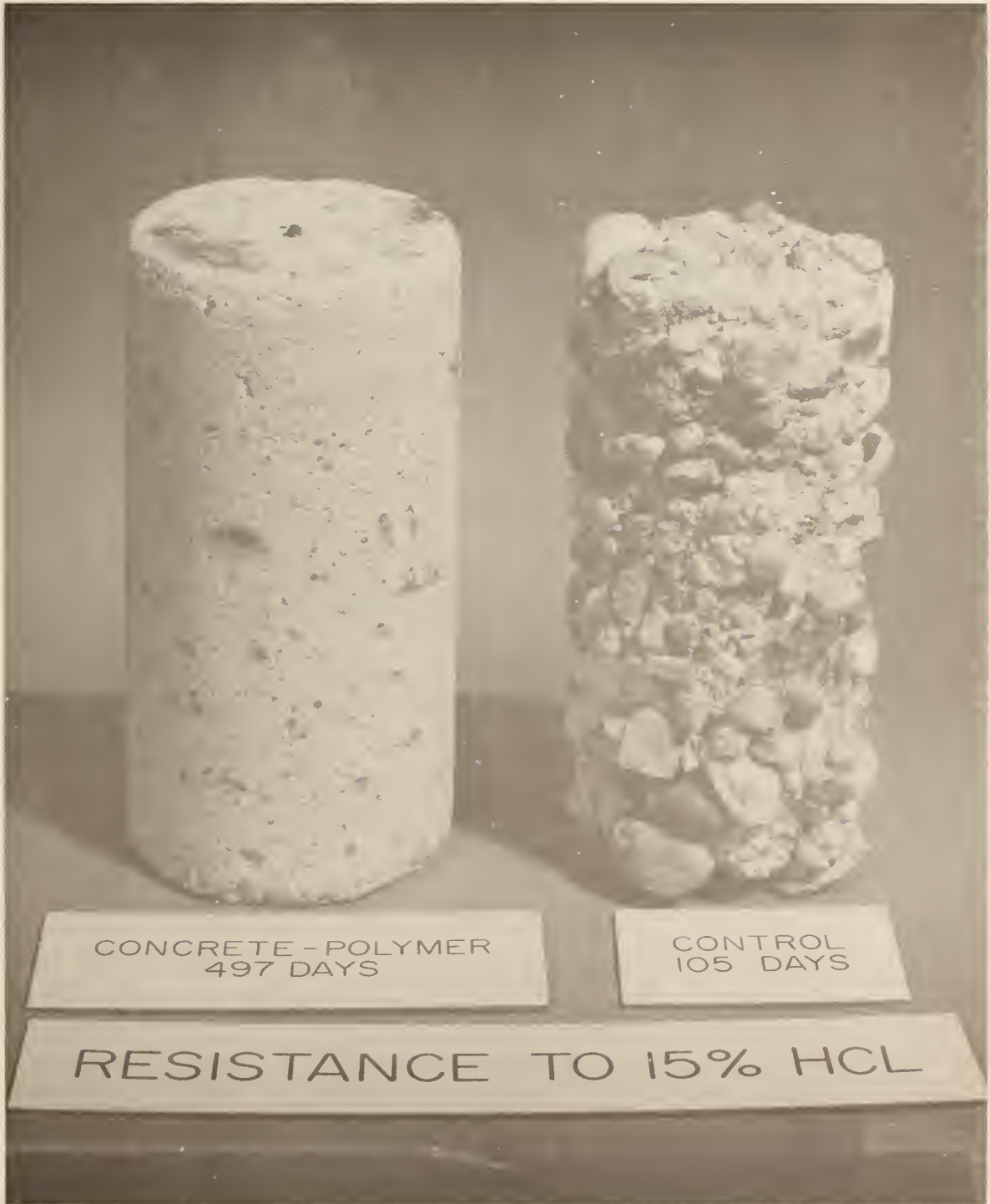
Figure 2-2. Resistance to Chemical attack (15% HCL). PIC lost 7% weight after 497 days. Control lost 25% in 105 days.
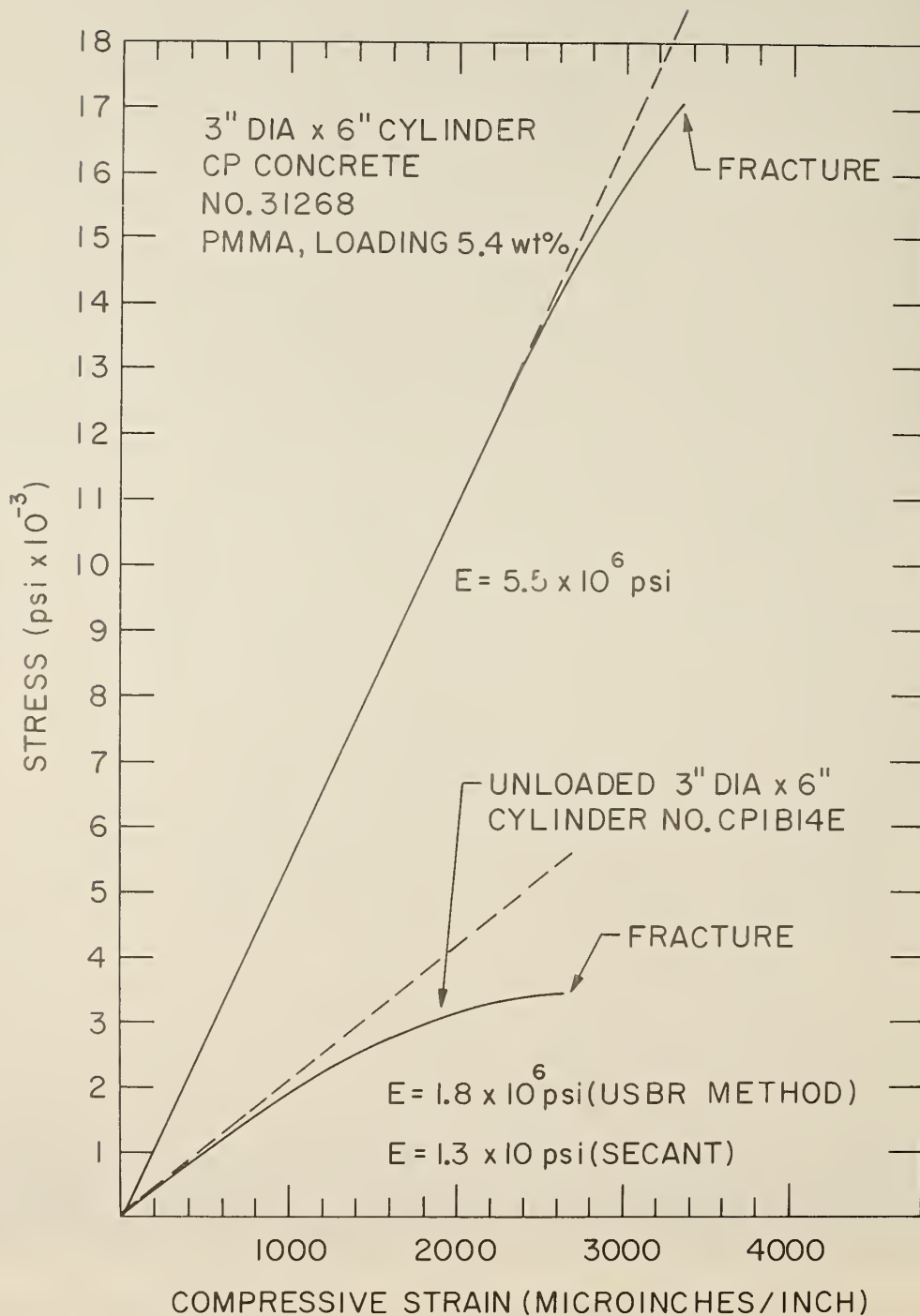
5

Figure 2-3. Compressive stress-strain curve for PMMA-impregnated concrete. Impregnated concrete shows elastic behavior; unimpregnated concrete shows plastic behavior.
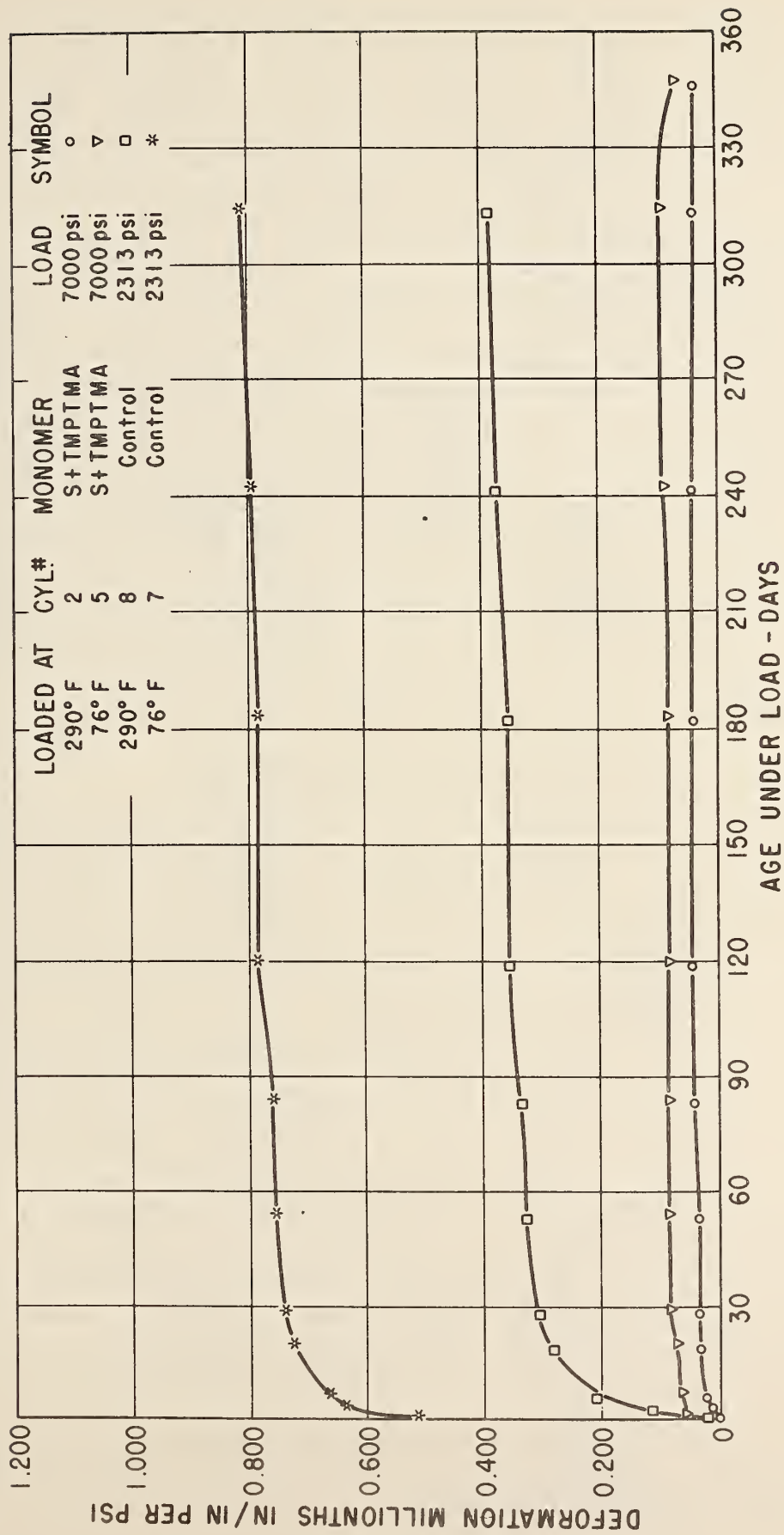
6

Figure 2-4. Creep strain characteristics of PIC.

PIC is produced by drying cured conventional concrete by the most convenient and economical processing technique (hot air, oven, steam, dielectric heating, etc.), displacing the air from the open cell void volume (vacuum or monomer displacement and pressure), diffusing a low viscosity monomer (<10 cP) through the open cell structure, saturating the concrete with the monomer and polymerizing the monomer in situ to a polymer by the most convenient and economical means (radiation, heat, or chemical initiation. Figure 2-5 is a schematic flow sheet of a process utilizing thermal-catalytic polymerization. Free-radical vinyl-type monomers, i.e., methyl methacrylate (MMA), styrene, acrylonitrile, tert-butyl styrene, and other thermoplastic monomers, are generally used in the production or PIC. For increased thermal stability, cross-linking agents and thermosetting monomers such as styrene-trimethylolpropane trimethacrylate (TMPTMA) and polyester-styrene are used. The more important process criteria are that the monomer should be of relatively low cost, readily available, and of relatively low viscosity. Much information on the formation and properties of PIC has been accumulated over the past five years in the U. S. [1-5] Table 2-1 gives a brief summary and classification of PIC materials and their properties. A U. S. patent has also been issued on the method of producting PIC. [6]

Polymer-Cement Concrete Materials Development

Polymer-cement concrete (PCC) is a premixture of hydrated cement paste and aggregate to which a monomer is added prior to setting and curing. The introduction of various organic materials to a concrete mix has been extensively investigated elsewhere [7] as well as at BNL. The improvements obtained in strength and durability are either disappointing or relatively modest. In many cases the resultant materials are inferior to concrete. Under the best conditions compressive strength improvements over conventional concrete of ∿50% are obtained if relatively high polymer concentrations, of the order of ∿30%, are used. Polyester-styrene, epoxy-styrene, furans, and vinylidene chloride have been used in PCC with limited success because most organic materials are incompatible with aqueous systems and in many cases polymerization either is inhibited by the alkalinity of the cement phase or interferes with the cement hydration process. In addition, porosity develops as a result of shrinkage during the curing process and many pores remain unfilled. With PIC, the polymer fills the voids and the strength, which is a function of the filled pore fraction, is therefore increased to a high degree.

The incentive to attain an improved premix concrete material is that it can be cast in place for field applications, whereas PIC requires a precast structure.
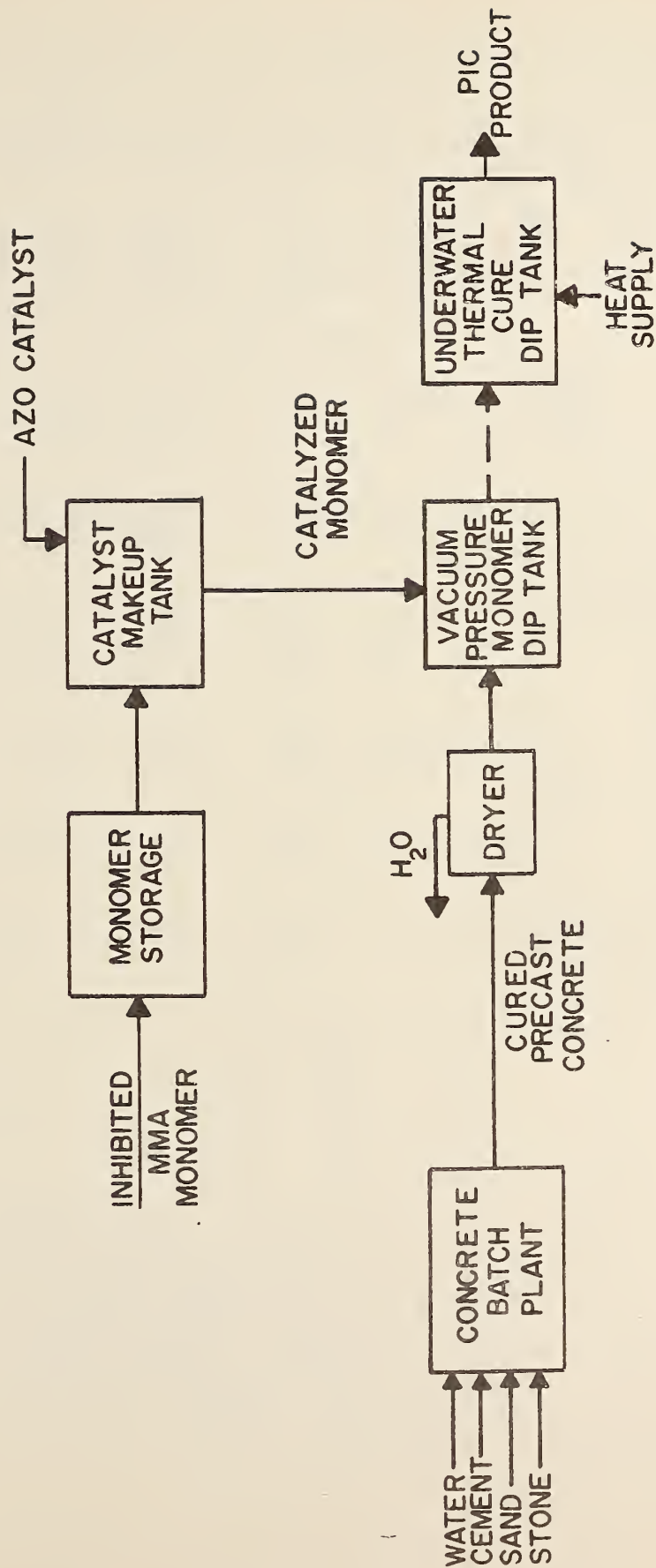
PRODUCTION OF POLYMER IMPREGNATED CONCRETE

PIC

Figure 2-5

9

Table 2-1

Classification of Concrete-Polymer Materials

	Polymer loading, wt % PMMA	Density lb/ft³	(gm/cc)	Compressive strength lbs/in.²	(Kg/cm²)	Strength to weight ratio	Durability	Benefit to cost ratio
1. Conventional concrete control	0.0	150	(2.40)	5,000	(353)	33	Poor	1.0
2. Surface Coating (SC) paint or overlay	0.0	150	(2.40)	5,000	(353)	33	Limited	1.1
3. Coating in Depth (CID)	1.0	150	(2.40)	6,000	(423)	40	Good	1.3
4. Polylmer Cement Concrete (PCC) premix								
a. Monomer premix	35.0	130	(2.08)	7,500	(528)	58	Fair	0.4
b. Polymer premix	1.0	150	(2.40)	10,000	(705)	49	Better	1.5
5. Polylmer Impregnated Concrete (PIC) Standard aggregate								
a. Undried-dipped	2.0	153	(2.45)	10,000	(705)	49	Fair	1.4
b. Dried-evac.-filled	6.0	159	(2.55)	20,000	(1410)	126	Very good	2.0
c. Hi-Silica steam cured	8.0	159	(2.55)	38,000	(2680)	240	Very good	3.0
Lightweight aggregate								
a. Struct. lt. wt. concr.	15.0	130	(2.08)	25,000	(1760)	193	Very good	2.5
b. Insul. lt. wt. concr.	65.0	60	(0.96)	5,000	(353)	84	Very good	2.5
6. Polymer Concrete (PC) cementless	6.0	150	(2.40)	20,000	(1410)	133	Excellent	4.0

A variation of PCC is the addition of a modest amount of polymer latex such as styrene-butadiene or polyvinylidene chloride emulsion to the fresh concrete mix. The amount of polymer added to the mix is less than 4% by weight of the total mix. Polymerization is not part of this process. The polymer particles coalesce during the concrete curing process and coat the pore structure of the concrete. The strength is improved by only a factor of 2, but durability is significantly increased.[8]

Polymer Concrete Materials Development

Polymer-concrete (PC) is an aggregate bound with a polymer binder. This material can be mixed and cast in the field. It is called a concrete because, by the general definition, concrete consists of any aggregate bound with a binder. The cheapest binder is portland cement, which costs about 1.25¢/lb in the U. S. Polymer can also be a binder; however, it is more costly than hydrated cement; price!s vary from 10¢/lb to 40¢/lb for the majority of commercial polymers. Because of the energy crisis, petrochemicals as well as cement have rapidly increased in cost during the past year.

Polymer filled with aggregate, for example, plastic containing powdered walnut shells, has long been used in table tops and furniture products. PC is an aggregate filled with a polymer. The main technique in producing PC is to reduce the void volume in the aggregate mass to minimize the quantity of the relatively expensive polymer needed for binding the aggregate. This is accomplished mainly by grading and mixing the aggregates. For example, to obtain a void volume <20%, an aggregate mix consisting of 3/8 - 1/2-in. stone (60.7 wt %), 20-30 mesh sand (23.0%), 40-60 mesh sand (10.2%), and 170-270 mesh sand (6.1%) is required. Conventional concrete mixing equipment can be used to prepare the mix. Safety precautions must be strictly observed when handling the flammable monomers.

There is another reason for furthering the development of PC materials. In conventional concrete, the alkaline portland hydraulic cement forms voids and cracks during hydration. Water can intrude and crack the concrete, and the alkaline cement is attacked by acidic media. With polymer as a binder, most of these difficulties are overcome. The polymer can be made compact with a minimum of open voids, and most polymers are hydrophobic and resist chemical attack. As shown in Table 2-1, the compressive strengths of PC can be as high as that of PIC (~20,000 psi). The monomer loadings are also comparable (6%).

A silane coupling agent can be added to the monomer to

improve the bond strength between the polymer and the aggregate. The main problems arise from the viscoelastic properties of the polymer. Polymers usually have a low modulus of elasticity, which means that they are flexible and exhibit creep. This is the primary reason why plastics are not used alone in structural members. By using polymer as a binder for aggregate, some of these difficulties are overcome and there is a good possibility of developing an important new class of materials with high benefit-to-cost ratios. It is known from the open literature that in the USSR[9] the development of PC is more advanced than in the U. S. Before PC is accepted as a reliable material of construction, much more investigation and experience will be required.

Aggregate Compositions

Consideration is now given to the aggregate in the binder-aggregate concretes or composites. The cheapest and most abundantly available aggregates are natural stone and sand, which are widely used throughout the world. There are a number of types and grades of stone aggregates which basically relate to igneous (granite), metamorphic (slate), and sedimentary (sandstone) stone. Aggregates are also classified as standard weight, structural lightweight, and insulating lightweight. Among the various lightweight polymer-impregnated concrete materials, perlite has been used to produce a material that is lighter than wood and compressively as strong as concrete. This opens up possibilities for producing lightweight, structurally strong mortars and concretes that are buoyant and have a high strength-to-weight ratio.

The properties of the various concrete-polymer materials produced to date are summarized in Table 2-1. The data include surface-coated (SC) and partially penetrated PIC (referred to as coated in-depth concrete, CID). The results of an attempt to combine the strength, durability, and manufacturing cost into a benefit/cost ratio for each of the materials are given in Table 2-1.

Urban Waste Utilization

Urban solid waste, such as garbage, refuse, sewage, paper, glass, and metal, can be used as aggregates. Sewage and solid-waste refuse polymer-impregnated concrete has been produced, with garbage used as the aggregate and sewage as the hydrating media for the cement. After curing, the concrete was dried, impregnated, and polymerized in situ with use of radiation. Compressive strengths as high as that of conventional concrete can be obtained (see Table 2-2).

Newsprint has been soaked in monomer and polymerized in situ under pressure to produce a material called paper polymer composite (PPC), or paper plywood. This composite has very good tensile strength along the plane of the paper (7500 psi).

Nonreturnable glass bottles have been crushed and graded and the mixed particulate glass filled with monomer in a manner similar to that used for PC. The polymer-bound broken glass is almost as strong as PIC and highly resistant to attack by corrosive media. The variously sized glass particles and a sample of the composite material are shown in Figure 2-6. An application of this material is for sewer pipe (Figure 2-7), especially when acid wastes are handled or when the hydrogen sulfide gas coming from sewage is oxidized under aerobic conditions to sulfuric acid. This material is called glass polymer composite (GPC). Conventional concrete is unsuitable for this environment; therefore asbestos cement and vitreous clay or cast iron pipe are usually specified.

Decorative bricks and facings for buildings can also be made from GPC. Incinerator ash has also been used as aggregate to produce a structurally sound material. Table 2-2 summarizes some of the properties of solid-waste-refuse polymer-concrete material. It is hoped that this materials development work will result in converting a negative ecological value into a positive asset in the form of valuable construction materials.

Applications Development

A number of applications for concrete polymer materials are being investigated. The Federal Highway Administration (FHWA) is sponsoring research to determine the feasibility of using prestressed PIC panels for bridge decking.[10] The Office of Saline Water (OSW) has been investigating the use of PIC for the construction of economical and durable distillation vessels for use in desalting plants. The Bureau of Mines (USBM) is investigating the chemical stabilization of coal mine roofs by impregnation of the stone[11] with monomers followed by in situ polymerization. The USBM is also developing a pumpable roof bolt.[12] PIC tunnel linings are another application of interest to the Bureau of Reclamation (USBR). The U. S. Navy has been interested in the use of PIC for underwater habitats and piling. PIC is also being considered for beams and building blocks for durable housing. The American Concrete Pipe Association (ACPA), in cooperation with the U. S. Atomic Energy Commission (US AEC) and the USBR, has investigated the use of PIC for sewer and pressure pipe. There is also interest in PIC railroad crossties. A number of industrial associations in the U. S. are investigating concrete-polymer materials for their own particular applications.

Table 2-2

Solid Waste and Sewage Containing Polymer Concrete

Type	Composition – wt. %				Compressive strength, psi	Tensile strength, psi
	Water	Portland Cement	Aggregate	Polymer[1] loading		
Standard concrete	6	14	80[4]	0	4,500	450
Sewage-cement concr.	38	46	16 solids[2]	0	2,200	–
Sewage-cement-polymer concrete	28	60	12 solids[2]	24	11,300	–
Refuse-cement-polymer concrete	17	33	50 refuse	10	4,000	–
Sewage-refuse-cement	18	28	54 refuse[2]	10	3,700	–
Glass-polymer composite[3] (GPC)	0	0	100 glass bottles	7	16,000	1,200
Paper polymer composite (PPC) paper plywood	0	0	100 newsprint	23	7,300	7,500

[1]Polymethyl methacrylate, wt. % of unloaded dried material
[2]Content of sewage sludge (70% water, 30% solids)
[3]Acid resistance 5 weeks, 5% H_2SO_4, 0.2% weight gain
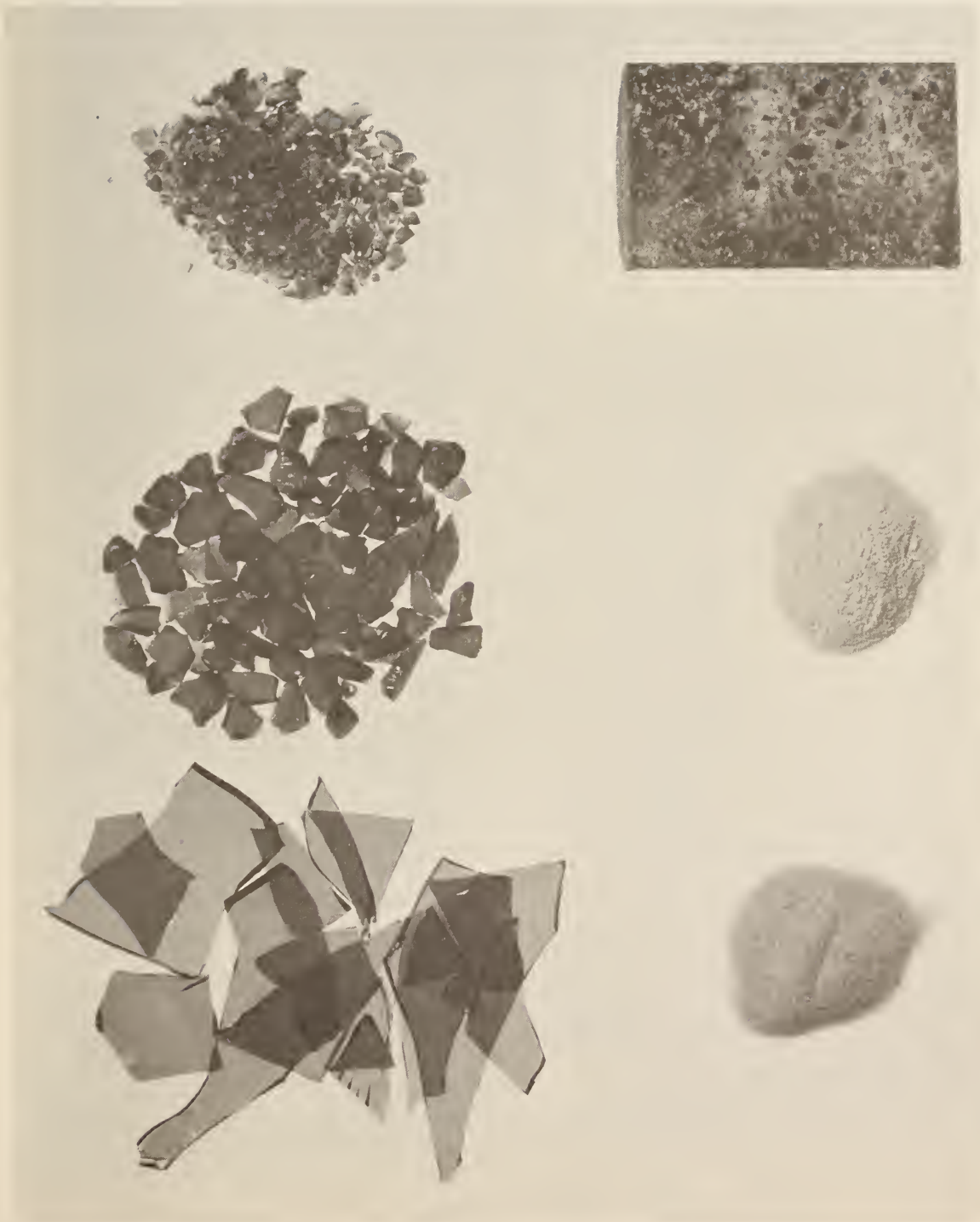Water absorption 5 weeks, no gain
[4]33% sand, 67% stone

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Figure 2-6. Glass-polymer composite showing mixtures of variously sized particles and specimen of GPC (lower right-hand corner). Composition: 90% waste glass, 10% styrene-polyester.

Figure 2-7. Glass-polymer composite pipe.

In Japan, a construction company in conjunction with a chemical company is reported to have constructed a 15 ton/day pilot plant for experimental production of PIC with use of thermal-catalytic initiation. The material has been named Powercrete, and beams, panels, and pipe have been produced.

A firm in the Union of South Africa is reported to have constructed a pilot plant for the thermal-catalytic production of PIC with use of a special type of concrete with smooth surfaces called mirror concrete. In addition to pipe and building concrete, a market for domestic sanitary ware such as wash basins, bathtubs, and sinks is being explored.

A cement association in Italy and the University of Rome are collaborating in developing PIC. They are using a high-strength concrete containing silica cement, high-pressure steam cured and polymerized under water. Possibilities exist for construction of ship plate and sewer pipe and for producing nuts and bolts and such items as screw-ended concrete sewer pipe.

Investigators in Norway, Denmark, Belgium, France, Spain, England, and Israel are exploring PIC applications, including heated road panels, curbing, base plates for pumps, and window sills.

Extensive work has been conducted in the USSR on developing and applying PC. The Russian literature[9] indicates significant advances in a number of applications, including tunnel supports.

A number of universities around the world have initiated studies on concrete-polymer materials.

Preliminary cost estimates indicate that PIC materials could be competitive with other conventional materials of construction. The feeling is that the field of concrete-polymer materials, in which an ancient materials technology (concrete) is combined with a new materials technology (polymer), is a growing and exciting one. Given the opportunity of additional investigation, demonstration, and experience, it is believed that concrete-polymer materials can become an important class of construction materials.

Storage of Nuclear Waste Materials

Another potentially important application for hydraulic cement concrete, in combination with the polymers in PIC and PC, is the storage of long-lived radioactive waste from the nuclear power industry. A major unsolved problem facing the exponentially growing industry is the safe disposal of fission product wastes. A technically and economically reasonable approach taken by the AEC is to immobilize the fission products in long-term durable materials in an engineered storage system. The material must be stored for 1000 years before it can be

considered biologically safe. Since it has been used in some environments for much longer periods of time, concrete appears to be an attractive material for accomplishing this goal. Further, concrete ingredients are low in cost and readily available. Adding the new dimension of PIC and PC can ensure additional durability and strength factors. The radioactive waste materials requiring storage are in the form of soluble salts, aqueous solutions (nitrates), oxides, glasses, and contaminated process equipment. The US AEC has established a program at BNL for investigating conventional concrete, PIC, and PC formulations for this application. The radiation stability, leachability, thermal stability, and structural integrity of promising formulations are being studied. Much more will have to be learned about these materials before it can be confidently predicted that they will last a thousand years or more. To date, mortars and concretes containing formulations of aqueous nitrates with calcium aluminates have been produced. After impregnation with styrene-divinyl benzene, they have shown radiation stability to 10^{10} rads. This is the total integrated radiation dose expected for 1000 years of exposure. Cross-linked polystyrene is especially radiation resistant. The compressive strength of these materials is ~13,000 psi.

CHAPTER III
INTRODUCTION TO POLYMER SCIENCE
Peter Colombo

Introduction

This chapter is an introduction to monomers and polymers for specific application to polymer-impregnated concrete (PIC) and polymer-concrete (PC) composites. It is intended to give highway engineers and field personnel a general understanding of the subject. The text is based on known concepts in polymer science and on the knowledge gained in laboratory and field experiments on concrete-polymer materials. Emphasis on some aspects of the subject reflect the thinking and experience of the author in relation to FHWA applications. A more thorough and complete treatment of the use of monomers and polymers for PIC and PC composites is provided in the references and in other chapters of the text.

1. Definitions

A monomer is a molecular species capable of combining chemically with molecules of the same or other species, to form a high molecular weight material known as a polymer.

A polymer consists of chains of repeating units derived from the interreaction of monomer units.

In general, the monomer is the starting material, and the polymer is the end product. The chemical process through which the conversion from monomer to polymer takes place is called polymerization.

When a monomer such as methyl methacrylate is polymerized, the process is called homopolymerization and the homopolymer polymethyl methacrylate is formed. When more than one chemical species, e.g., a mixture of methyl methacrylate and styrene, is polymerized, the process is called copolymerization and a copolymer is formed.

Figure 3-1 is a schematic representation of a homopolymer. Each small circle in the polymer chain represents a monomer molecule. During the reaction, the monomer molecules chemically attach themselves to one another to form chains that are very long and flexible and become entangled during polymerization. The illustration in Figure 3-1 represents a homopolymer, since all the molecules that make up the polymer chains are alike. Examples of homopolymers are polystyrene and polymethyl methacrylate. Polymer chains consist of thousands of monomer units, all chemically tied together. The mechanical and thermal properties of many polymers are dependent on the length of the polymer chains.
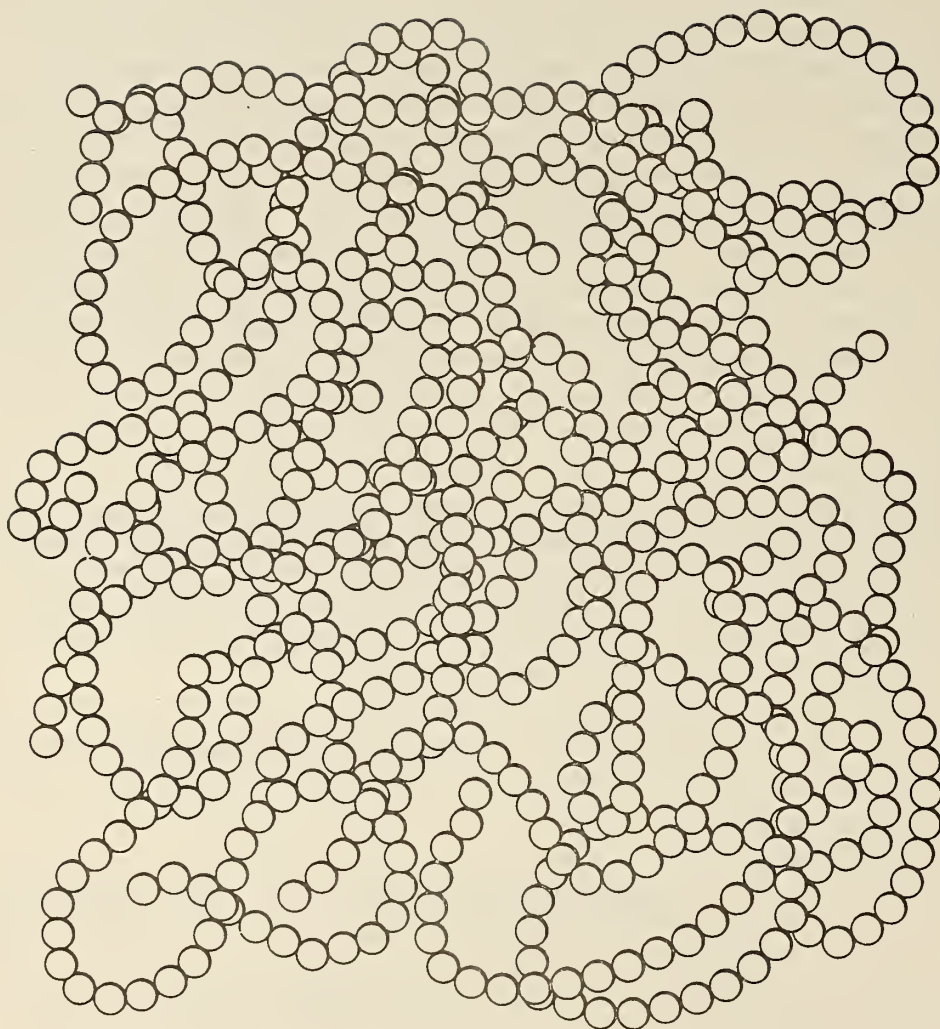
Figure 3-1

A schematic representation of a polymer. The spheres
represent the repeating units of the polymer chains

Copolymers can be made in a number of different geometric arrangements, some of which are illustrated in Figure 3-2. The most common configuration resulting from copolymerization involving two monomer species is a <u>random</u> <u>copolymer</u>. During polymerization, the monomer molecules add along the chain in a random manner, as indicated by the light and dark circles in Figure 3-2. <u>Alternating copolymers</u> are formed as a result of a strong tendency for the monomer molecules to alternate during polymerization. <u>Block</u> <u>copolymers</u> (Figure 3-2) consist of alternating sequences of homopolymers chemically bound to form long polymer chains. <u>Graft</u> <u>polymers</u> are those made by "grafting" chains of one polymer onto a "backbone" of a second polymer by means of chain transfer reactions.
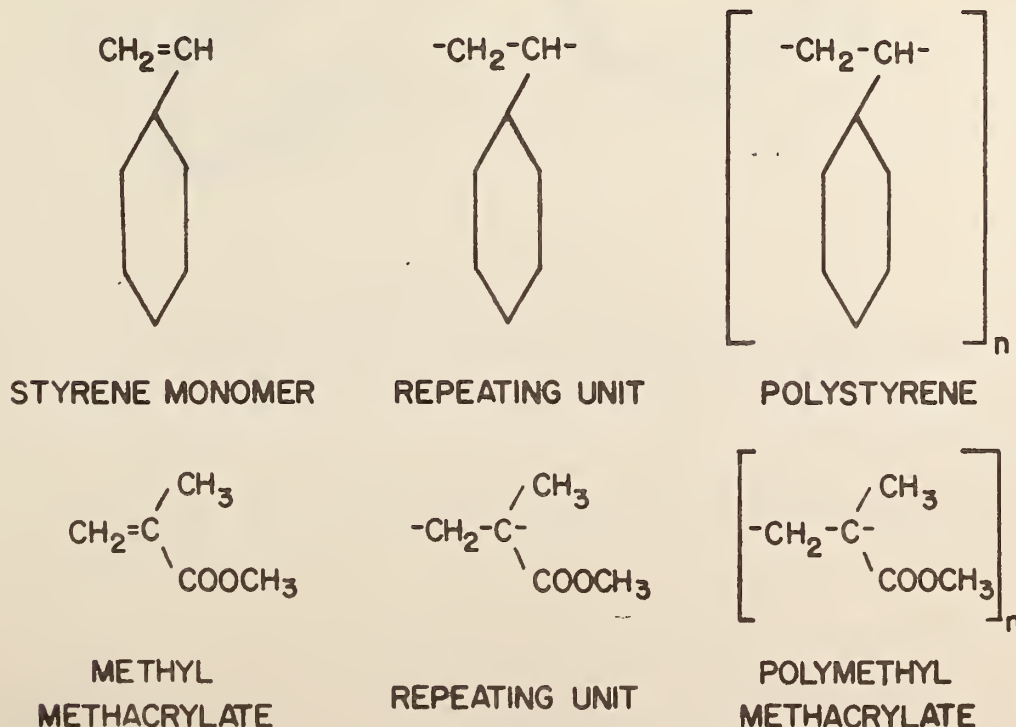
Homopolymers have specific mechanical and chemical properties. By combining homomonomers in the proper proportion, copolymers having the most desirable properties for a specific application can be formed. More complete information on definitions in polymer chemistry can be found in Refs. 13 and 14.

2. <u>Polymerization</u> <u>Processes</u>

The processes of polymerization are divided into two groups known as addition and condensation polymerizations.

<u>Addition</u> <u>Polymerization</u>

An addition polymerization process is one in which the monomer molecules combine through the formation of free radicals. This process is characteristic of vinyl monomers that contain the grouping $-CH=CH-$. A typical addition polymerization process involving styrene and methyl methacrylate is as follows:

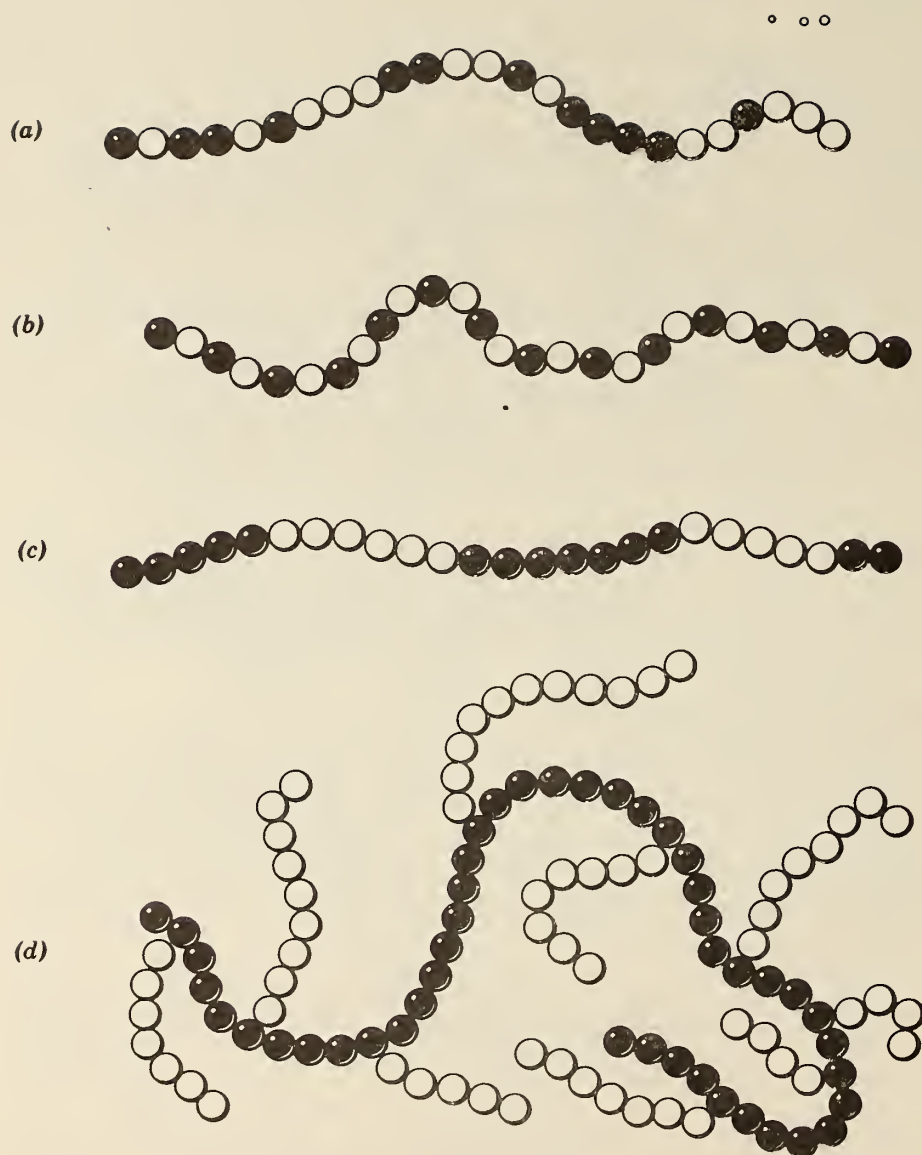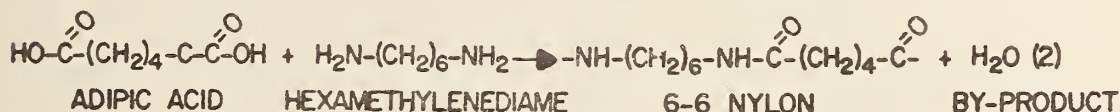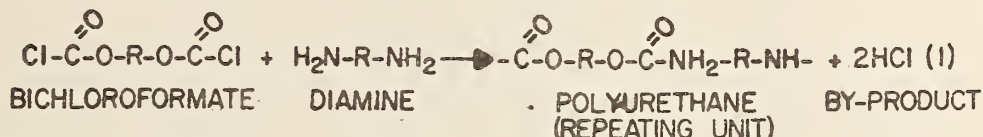| STYRENE MONOMER	REPEATING UNIT	POLYSTYRENE
METHYL METHACRYLATE	REPEATING UNIT	POLYMETHYL METHACRYLATE

Figure 3-2

Copolymer arrangements
(a) a random copolymer, (b) alternating copolymer,
(c) a block copolymer, (d) a graft copolymer

Styrene and methyl methacrylate monomers react through the double bond to form long chains of homopolymer having the same repeating unit. In the above process only polymer is formed. There are no by-products to be eliminated.

Condensation Polymerization

This process involves the reaction between two monomer molecules, which are usually chemically different, to form a new chemical bond between the two. The molecular formula of the repeating unit is different from that of the monomer. Two examples of the condensation process are given below.

$$Cl\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}O\text{-}R\text{-}O\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}Cl \; + \; H_2N\text{-}R\text{-}NH_2 \longrightarrow \text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}O\text{-}R\text{-}O\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}NH_2\text{-}R\text{-}NH\text{-} \; + \; 2HCl \; (1)$$

  BICHLOROFORMATE   DIAMINE   POLYURETHANE   BY-PRODUCT
                                              (REPEATING UNIT)

$$HO\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}(CH_2)_4\text{-}C\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}OH \; + \; H_2N\text{-}(CH_2)_6\text{-}NH_2 \longrightarrow \text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\shortparallel}{C}}\text{-} \; + \; H_2O \; (2)$$

  ADIPIC ACID   HEXAMETHYLENEDIAME   6-6 NYLON   BY-PRODUCT

For applications in polymer-concrete and polymer-impregnated concrete, condensation reactions are difficult to perform since extremely high temperatures and acid-type catalysts are usually required to initiate the reaction. In addition, the by-product elimination inherent in most of these reactions is detrimental to the composite. More detailed descriptions of addition and condensation polymerization processes are given elsewhere.[15,16]

Addition-Type Monomers

Under normal conditions of temperature and pressure, monomers are in the form of liquids, solids, or gases. Several addition-type monomers are listed in Table 3-1. The liquid-type monomers in the table are those that have been considered by BNL to be most suitable for the impregnation of precast concrete and for the production of polymer concrete composites.[2-4] Solid-type monomers are not used since they can be added to a mix only as aggregate and therefore do not fill the voids and capillaries formed during hardening of the concrete. Since their bonding properties with sand or other aggregates are poor, they cannot be used for producing polymer-concrete composites. Gaseous-type monomers have been used for impregnating precast concrete.[2,3] Although the test results were satisfactory, the techniques and equipment required are impractical, particularly for field application.

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Table 3-1

Forms of Monomers

(under normal conditions of temperature and pressure)

Liquids	Solids	Gases
Styrene	Acrylamide	Ethylene
Methyl methacrylate	Vinyl stearate	Vinyl chloride
Polyester-styrene	Sodium methacrylate	Tetrachloroethylene
Trimethylolpropane Trimethacrylate (TMPTMA)		

3. Monomer-Polymer Properties

The monomers that have been used for FHWA applications and some of their most important physical properties are given in Table 3-2. Based on the viscosity values shown, all the monomers can be used for polymer-concrete composites. Styrene or methyl methacrylate can be used alone or in combination with trimethylolpropane trimethacrylate (PMPTMA). Polyester-styrene can be used as is, or it can be further diluted with styrene monomer to decrease viscosity. With the exception of polyester-styrene, which has a high viscosity, the monomers listed in Table 3-2 can also be used for impregnating precast concrete. The high boiling points and low freezing points of these monomers give them great applicability over a wide range of temperature conditions.

The flash points and explosive limits of the monomers in air are also given in Table 3-2. The <u>flash point</u> is defined as the temperature at which a liquid gives off a sufficient amount of vapor to form an ignitable mixture with air near the surface of the liquid or within a container. The explosive limits are given as the upper and lower limits of vapor concentration in air at room temperature and atmospheric pressure that will support combustion.

Mechanical Properties of Polymers

The tensile, compressive, and flexural strengths for polystyrene, polymethyl methacrylate and polyester-styrene are given in Table 3-3. These properties exhibit wide ranges and depend on many conditions such as impurities, polymerization temperature, catalyst concentration, and catalyst type.

Chemical Stability of Polymers

Important properties of polymers are resistance to acidity, alkalinity, and solvents. The effects of these materials on polystyrene, polymethyl methacrylate, and polyester-styrene are summarized in Table 3-4. Sunlight tends to oxidize the surface of polystyrene and polyester-styrene, which results in a slight discoloration. This effect is not detrimental to the overall properties of the polymers. The effect of sunlight on polymer-impregnated concrete and polymer-concrete composites containing these polymers is negligible, since the amount of polymer on the surface of the composites is small. As indicated in Table 3-4, all the polymers are resistant to weak acids. Strong acids, particularly the oxidizing types such as nitric and hydrochloric acid attack polystyrene and polymethyl methacrylate. Weak alkalines have no effect on the polymers, but strong alkalines

Table 3-2

Monomer Properties

Monomer	Viscosity cps	Boiling Point °C	Freezing Point °C	Flash Point °C	Explosive Limits Vol % in Air
Styrene	0.76	145	-30.6	34.4	1.5-7.0
Methyl Methacrylate	0.85	101	-48.0	21.1	2.1-12.5
Trimethylolpropane Trimethacrylate (TMPTMA)	50.0	-	-14.0	>300	-
Polyester-Styrene	400-2,000	(a)	(a)	34.4	1.5-7.0

(a) Values are dependent upon the relative amount and type of polyester base.

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Table 3-3

Mechanical Properties of Polymers

Polymer	Tensile Strength psi	Compressive Strength psi	Flexural Yield Strength psi
Polystyrene	5,000-12,000	11,500-16,000	8,000-14,000
Polymethyl-Methacrylate	8,000-11,000	11,000-19,000	12,000-17,000
Polyester-Styrene	6,000-13,000	13,000-26,000	8,500-23,000

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Table 3-4

Resistance Characteristics of Polymers

Property	Polymer		
	Polystyrene	Polymethyl Methacrylate	Polyester-Styrene
Effect of sunlight	Yellows slightly	Nil	Yellows slightly
Effect of weak acids	None	Nil	None
Effect of strong acids	Attacked by oxidizing acids	Attacked only by high concentrations oxidizing acids	None to slight
Effect of weak alkalis	None	Nil	None to slight
Effect of strong alkalis	None	Attacked	Attacked
Effect of organic solvents	Soluble in aromatic and chlorinated hydrocarbons	Soluble in aromatic and chlorinated hydrocarbons	Attacked by ketones and chlorinated solvents

such as concentrated sodium hydroxide attack polymethyl methacrylate and polyester-styrene. Organic solvents dissolve polystyrene and polymethyl methacrylate. The polyester-styrenes may be attacked causing a small amount of degradation but they do not dissolve since they are cross-linked polymers which are highly resistant to solvents.

Cross-Linking Agents

Homopolymers of styrene and methyl methacrylate consist of tightly packed polymer chains held together by Van der Waals forces. At high temperature, thermal motion overcomes the physical bonds (Van der Waals forces) between chains, and the chains slip past one another. The polymer goes from a hard glassy material to a rubbery or flowable liquid. On cooling, the polymers revert to their original form. When an appropriate solvent is added to these polymers, it penetrates the interface between polymer chains and thus reduces the physical forces; this allows the chains to slip past one another and go into solution. Such polymers are called thermoplastics.

It is also possible to link the polymer chains of thermo-plastics with strong chemical bonds through the use of cross-linking agents. Cross-linking agents are polyfunctional compounds capable of taking part in two separate addition reactions simultaneously to form a three-dimensional network. The cross-linking agent used at BNL for improving the thermal and solvent resistant properties of polystyrene and methyl methacrylate is trimethylolpropane trimethacrylate (TMPTMA).

Two cross-linking arrangements are shown in Figure 3-3. The upper arrangement (Figure 3-3a) shows cross-linked polymer chains in which small chain segments consisting of polymer-like molecules act as cross-links between the main polymer chains. The lower arrangement is one that is produced when a single molecule binds the segments of the main polymer chain. The degree of cross-linking and the arrangement depend on the nature of the polymer chains and on the type and concentration of cross-linking agent.

4. Free-Radical Polymerization

The polymerization of unsaturated monomers such as styrene, methyl methacrylate, and polyester-styrene is typically a chain reaction. Polymerization can be initiated by the action of a free radical on a monomer molecule, which may lead to polymer chains consisting of thousands of monomer molecules. Free radicals can be formed by the decomposition of a relatively unstable material called an initiator or a catalyst. Figure 3-4 describes the mechanism involved for a free-radical-initiated addition polymerization. The initiator molecule, shown in Figure 3-4, is benzoyl peroxide, a commonly used initiator.
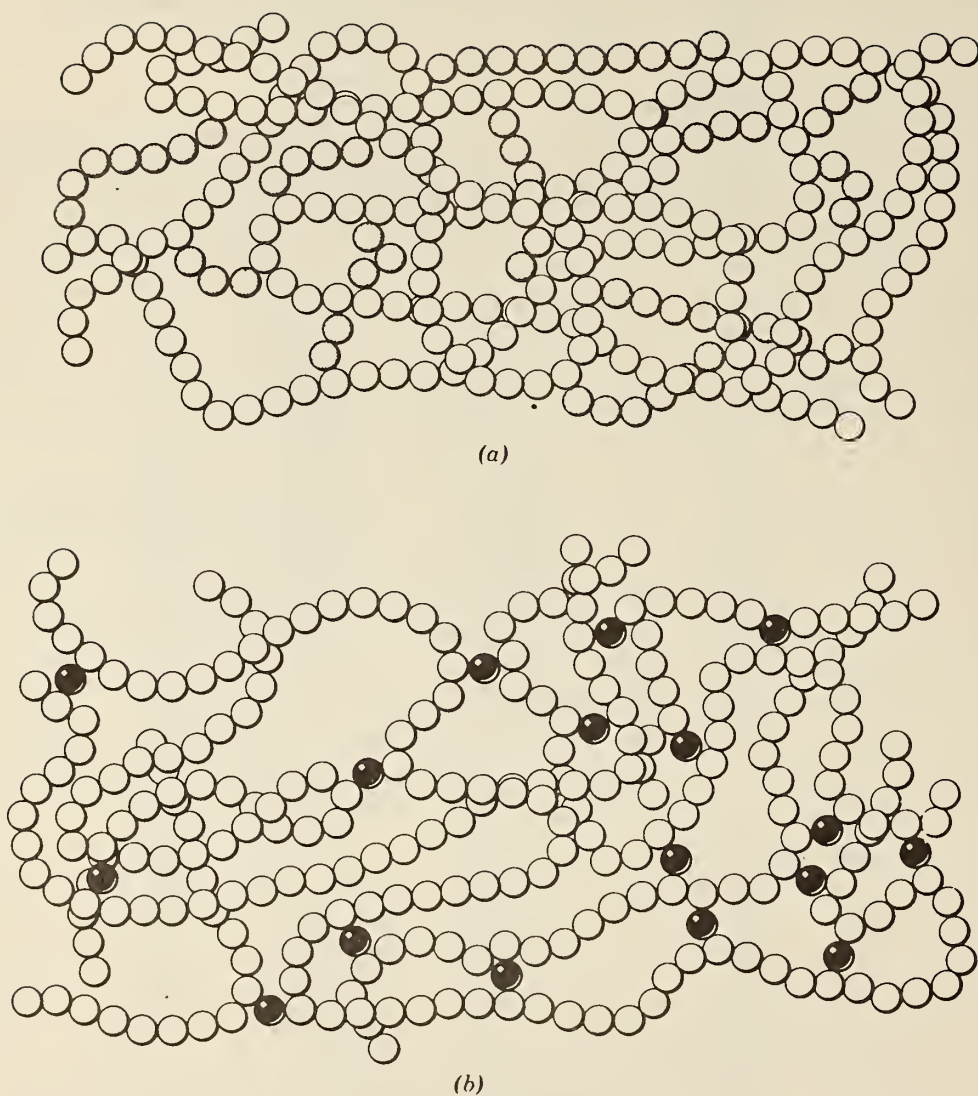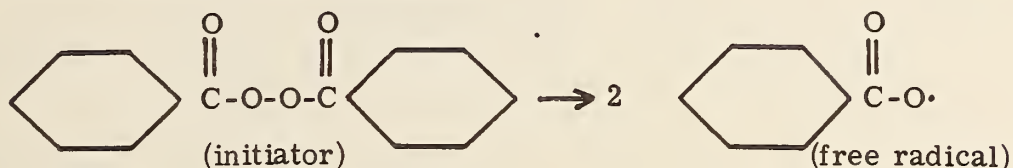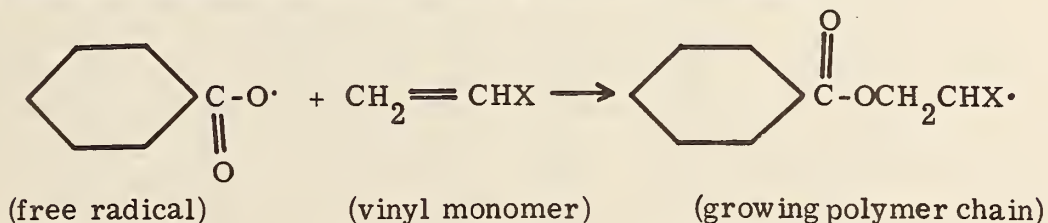
(a)

(b)

Figure 3-3

Cross-linking arrangements
(a) cross-linked polymer chains in which small chain
segments act as cross-links, (b) cross-linked polymer
chains in which foreign atoms or molecules are the cross-links

Addition Polymerization

Free radicals are formed by the decomposition of a relatively unstable material called an <u>initiator</u>

The free radical is capable of reacting to open the double band of a monomer and add on, regenerating the unpaired electron:

Monomers add successively to the growing chain in a matter of seconds. Finally two free radicals combine to terminate polymer chain growth.
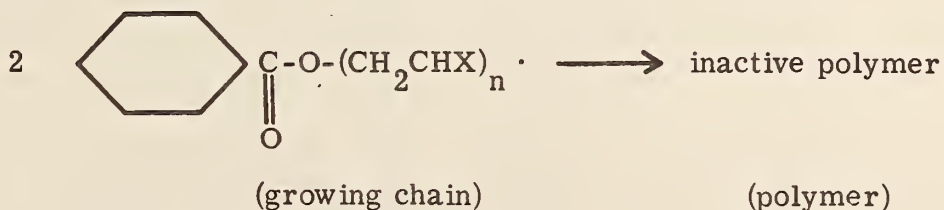

Figure 3-4

When subjected to heat or in the presence of a promoter, the molecule splits at the O-O bond to form two free radicals that have unpaired electrons and are thus very reactive. A formed free radical attacks a monomer molecule, the double bond is broken, and a monomer molecule with an unpaired electron is produced. The new free radical seeks out another monomer molecule, the sequence is repeated, and the result is a growing polymer chain. The growing chains end when all the monomer is consumed or when two growing chains meet end to end. Many of these reactions take place at the same time. The rate of polymerization can be controlled by varying the initiator (catalyst) concentration and or the temperature. In general, the lower the initiator concentration and temperature, the lower the polymerization rate.

Promoters can be used instead of temperature for room-temperature curing of some catalyzed monomer systems. Promoters (also called accelerators) are chemical compounds that induce the decomposition of a peroxide catalyst by breaking the O-O bond. This reaction can take place over a very wide temperature range, depending on the promoter-catalyst system used. For normal temperature use, the promoter-catalyst combinations listed in Table 3-5 yield the best results. These systems allow a reasonable working time before the mixture sets or becomes unworkable. The concentration, of promoter and catalyst for a given mix affect the cure time. The effect of concentration on cure time for polymer-concrete composites is discussed in Chapter V and Appendix A. If a temperature cure is preferred to a promoter-catalyst cure, the same catalysts (Table 3-5) can be used for initiating the polymerization reaction. The temperature requirements for thermal-catalytic polymerization vary with catalyst. This is also discussed in Chapter V.

5. Plasticizers

Plasticizers can be defined as chemically and thermally stable organic materials used to modify the physical properties of polymers. In most applications, plasticizers are used to impart flexibility, which the polymer in its original state does not have.

As discussed previously, polymers consist of a series of long, threadlike chains, more or less randomly arranged. For the polymer to be flexible and extensible, the polymer chains must be free to slide past one another. In an unplasticized state, this relative motion of the chains is restricted because of the physical or Van der Waals forces between the polymer chains and to mechanical entanglement. The strength of these bonds determine the rigidity or flexibility of the polymer. When plasticizers are added to the polymer, they act to loosen the bonds between polymer chains by neutralizing the physical

Table 3-5

Promoter-Catalyst Systems Used for "Room Temperature" Curing

Monomers	Catalyst	Promoter
Polyester-styrene	Methyl ethyl ketone peroxide	Cobalt naphthenate
Methyl methacrylate	Benzoyl peroxide	Dimethyl aniline + dimethyl toluidine
Methyl methacrylate + TMPTMA (a)	Benzoyl peroxide	Dimethyl aniline
Styrene + TMPTMA	Benzoyl peroxide	Dimethyl aniline

(a) Trimethylolpropane trimethacrylate

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forces and thus allow the chain to slide past each other more easily.

The polymers used for FHWA applications (Table 3-3), can be classified as strong and brittle materials. In forming polymer-impregnated concrete and polymer-concrete composites, the sand and stone aggregate, and the portland cement concrete used in the formulations can also be classified as strong and brittle materials. These composites can fail catastrophically under certain conditions of stress or impact. If plasticizers are used to improve the flexibility or resilience, the composite will be capable of absorbing higher impact loads.

Plasticizers can generally be divided into two types, known as external and internal plasticizers. The external type does not enter into a chemical reaction with the polymer and can eventually migrate out of the polymer, depending on time and on the environmental conditions. When this occurs, the polymer properties approach those of its original state.

Plasticizers of the internal type are more desirable, since they become an integral part of the polymer chain through chemical reaction. These materials are usually monomers which polymerize to form very flexible homopolymers. Addition of these monomers to a base monomer such as styrene, methyl methacrylate, or polyester-styrene prior to polymerization results in copolymers with mechanical properties different from those of their respective homopolymers. Figure 3-5 shows the effect of a plasticizer on the compressive stress-strain characteristics of a polymer-concrete composite containing methyl methacrylate. The composite is an elastic material over the range of stress indicated by the linear portion of the curve. The breaking stress, taken where curve a ends, is only a few percent from that of the yield stress (where the curve departs from the linear portion of the curve). Addition of 5% butyl acrylate had little effect on the stress-strain properties of the composite (curve b). A significant effect was noted when 20% butyl acrylate was added to the base monomer. Curve c indicates a more ductile material having a higher impact strength than that of the base monomer. This is indicated by the shape of the stress-strain curve: the break point is well beyond that of the yield point.

The use of plasticizers in polymer-concrete composites can extend the use of these materials to applications in which impact load is an important criterion. Since the binder for a polymer-concrete material is the polymer, the mechanical properties of the composite can be varied to reflect those of the polymer. The effects of plasticizers are less pronounced for polymer-impregnated concrete, where the cement phase is a binder. The polymer loadings (~6 wt %) are too low to exert any significant change on the plasticity of the composite.
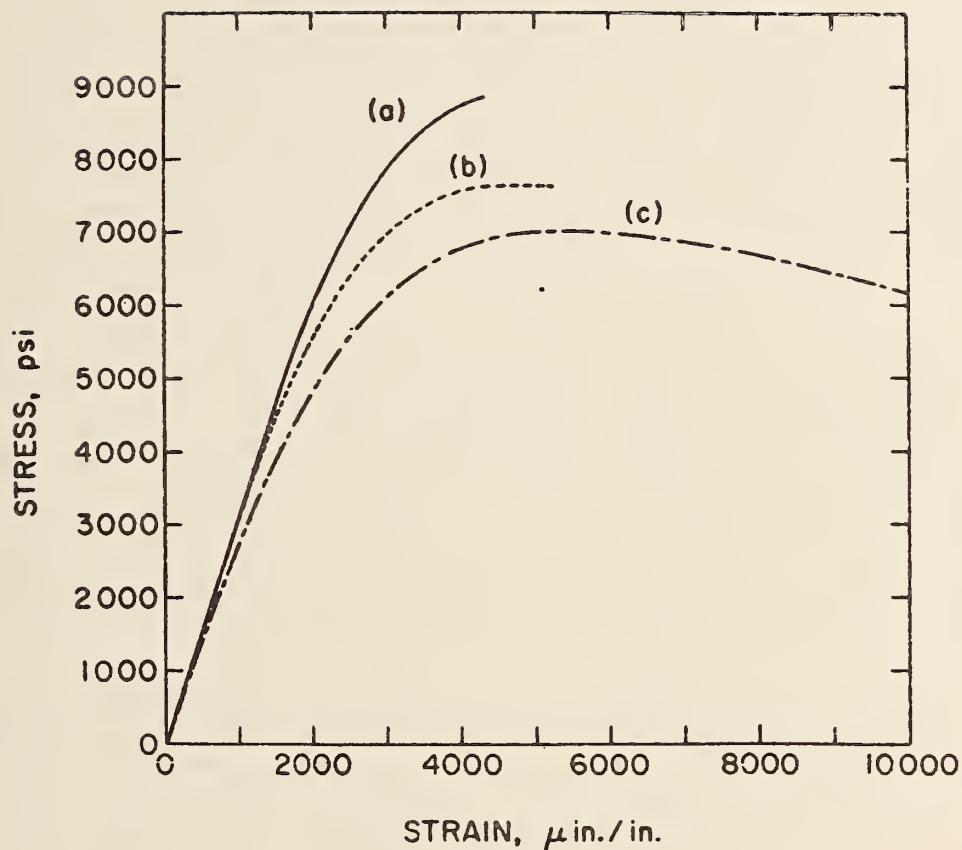
Figure 3-5 Compressive stress-strain curves for polymer-concrete. Curve *a*, MMA; curve *b*, 95 wt % MMA – 5 wt % butyl acrylate; curve *c*, 80 wt % MMA – 20 wt % butyl acrylate.

6. Silane Coupling Agents

Two types of bonding can take place when a monomer is polymerized in the presence of sand or other silica-containing aggregate. One type involves a chemical bond at the interface between the inorganic substrate and the organic polymer. The second type is physical bonding, in which the polymer and aggregate are held together by Van der Waals forces.

Most of the stress in a polymer-impregnated concrete or in polymer-concrete is carried by the aggregate or cement phase. The polymer matrix serves to distribute the load over as wide an area as possible by filling cracks, voids, and other discontinuities that occur during formation of the composite. This type of load spreading requires that the stress be transferred across the interface between aggregate and polymer. Stress can be transferred between the two materials only if they are in intimate molecular contact. If separation occurs, even at the molecular level, as a result of shrinkage, temperature, water intrusion, or for any other cause, the ability to transfer stress is decreased appreciably. Bond energies resulting from chemical bonds are ~20 to 150 kcal/mole, an order of magnitude higher than those of physical bonds. It therefore appears that chemical bonds are preferred over physical bonds. Tests[5] have indicated that the type of bonding that normally takes place between polymer and siliceous materials is a physical bond.

Chemical bonding can be induced by use of silane coupling agents. These agents consist of molecules having two different types of reactivities. One portion of the molecule is organic and is capable of reacting with a variety of monomers. The other portion is inorganic and reacts with silica to form a chemical bond.

The reactions that take place between silane coupling agents, sand, and polymer are illustrated in Figure 3-6. Upon exposure to moisture, γ-methacryloxypropyl trimethoxysilane (a coupling agent) forms a silanol which reacts rapidly with silica to form a chemical bond. In the presence of a monomer such as methyl methacrylate and a chemical initiator, the organic portion of the molecule reacts by a free-radical mechanism to form long polymeric chains.

The methods that can be used to apply silane coupling agents to polymer-impregnated concrete and polymer-concrete composites are given in Table 3-6. The simplest method and the one currently being used for FHWA applications is that in which the silane is mixed with the monomer prior to contact with sand or precast concrete. However, as indicated by the compressive strength values given in Table 3-6, this method is not the most efficient.
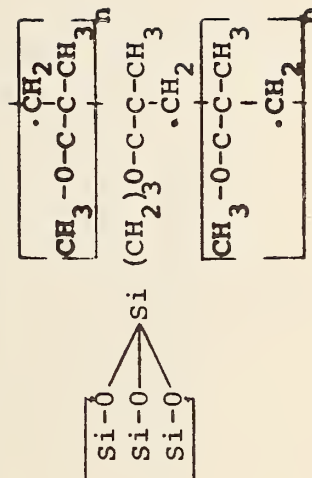
SILANE COUPLING BETWEEN SAND AND MONOMER

$$CH_2=CCH_3\overset{O}{\overset{\|}{C}}O(CH_2)_3Si(OCH_3)_3 \xrightarrow{H_2O} CH_2=CCH_3\overset{O}{\overset{\|}{C}}O(CH_2)_3SI(OH_3)_3+CH_3OH$$

γ – methacryloxypropyltrimethoxysilane ⟶ silanol

$$\begin{bmatrix} Si-OH \\ Si-OH \\ Si-OH \end{bmatrix} + CH_2=CCH_3\overset{O}{\overset{\|}{C}}O(CH_2)_3Si(OH_3)_3 \longrightarrow$$

$$\begin{bmatrix} Si-O \\ Si-O \\ Si-O \end{bmatrix}Si(CH_2)_3O\overset{O}{\overset{\|}{C}}CH_3C=CH_2+3H_2O$$

$$\begin{bmatrix} Si-O \\ Si-O \\ Si-O \end{bmatrix}Si(CH_2)_3O\overset{O}{\overset{\|}{C}}CH_3C=CH_2 + CH_2=CCH_3\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow{\text{Radiation}}$$
or
Chemical Catalyst

$$\begin{bmatrix} Si-O \\ Si-O \\ Si-O \end{bmatrix}Si(CH_2)_3O-C-C-CH_3 \cdot CH_2 \begin{bmatrix} \cdot CH_2 \\ | \\ CH_3-O-C-C-CH_3 \end{bmatrix}_n \begin{bmatrix} \cdot CH_2 \\ | \\ CH_3-O-C-C-CH_3 \\ | \\ \cdot CH_2 \end{bmatrix}_n$$
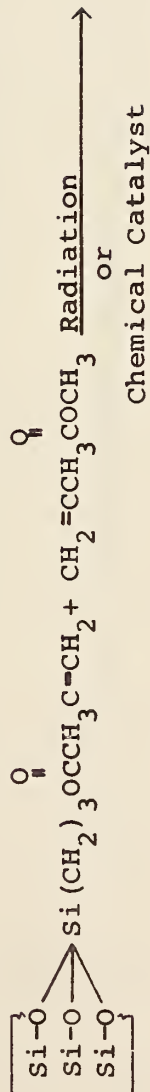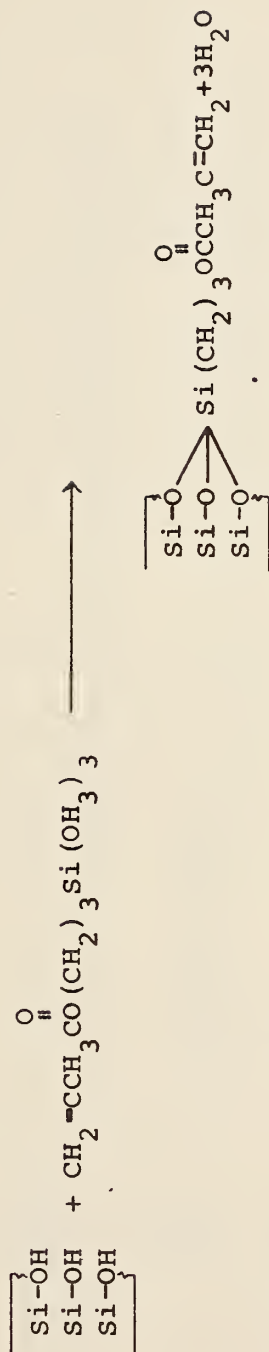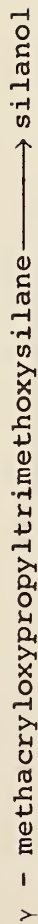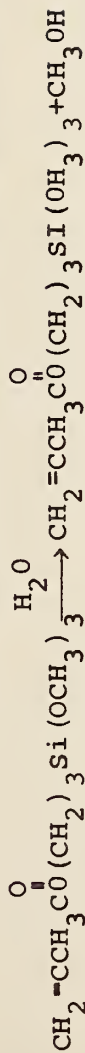
Figure 3-6

Table 3-6

EFFECT OF METHOD OF SILANE COUPLING APPLICATION ON
COMPRESSIVE STRENGTH OF POLYMER-CONCRETE

Sample No.	Compressive strength psi	Method of silanization
1	13,875	1% by weight of silane blended with MMA prior to contact with aggregate and sand[a]
2	13,790	
3	13,800	
4	15,750	Aggregate and sand were treated with 1% silane hydrolyzed in water, dried, and contacted with MMA
5	15,825	
6	15,790	
7	15,900	Aggregate and sand were exposed to silane vapor before contact with MMA
8	16,150	
9	16,000	
10	11,200	No silane coupling agent added
11	10,950	
12	10,750	

(a) Union Carbide A-174 γ-methacryloxypropyltrimethoxysilane.
MMA = methyl methacrylate.

The effectiveness of silane coupling in polymer-concrete composites is further demonstrated in Figure 3-7. Polymer-concrete specimens prepared with and without a silane coupling agent were subjected to tensile splitting tests. The upper specimen, prepared without the use of a coupling agent, failed primarily because of the poor bond between the polymer and aggregate. This is indicated in Figure 3-7 by the voids created by the dislodgment of the aggregate from its bedding. The lower specimen, prepared with a coupling agent, failed because of fracture of the stone aggregate. In this specimen the polymer-aggregate interface remained essentially intact.

Polymer-concrete specimens prepared with and without a coupling agent were exposed to boiling benzene for 24 hr. Benzene is a strong solvent for the methyl methacrylate used as the base monomer for these composites. The results of this test are shown in Figure 3-8. The polymer in the composite that did not contain silane completely dissolved away from the aggregate. The polymer in the composite containing silane did not dissolve, and the specimen retained its original configuration.
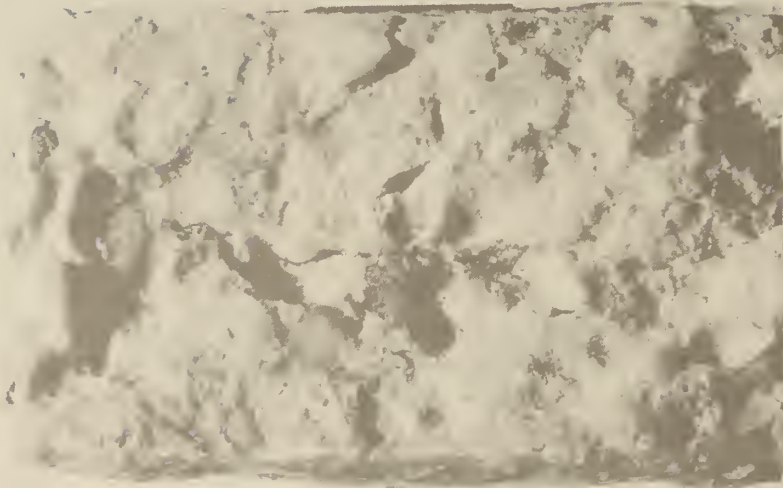
7. Flammability

All organic materials, including polymers, burn vigorously in the presence of oxygen. However, materials can be added to monomers and polymers to reduce the flammability. These materials mainly contain chlorine, bromine, antimony, and phosphorous. To be effective as flame retardants, large concentrations of these materials are generally required. This normally has an adverse affect on the mechanical properties of the polymer.

A series of flammability tests was performed to determine the relative burning rates for polymers, polymer-impregnated concrete, and polymer-concrete composites.[5] The flame test, designated ASTM-D-635-68, measures the relative burning rates of self-supporting plastics. The apparatus for this test is shown in Figure 3-9. In accordance with the test, a flame is played on one end of the specimen for 30 sec. The flame is then removed and the burning rate is measured. Figure 3-10 shows the results of a test in which the material proved to be self-extinguishing. The results of tests on various composite materials are given in Table 3-7. With the exception of chloro-styrene, all the homopolymers were rated as flammable by this test. The chlorine component in the chlorostyrene molecule constitutes a "built-in" flame retardant.

The burning characteristics of polymers incorporated into polymer-impregnated concrete and polymer-concrete composites are drastically different from those for homopolymers. Under the

POLYMER CONCRETE
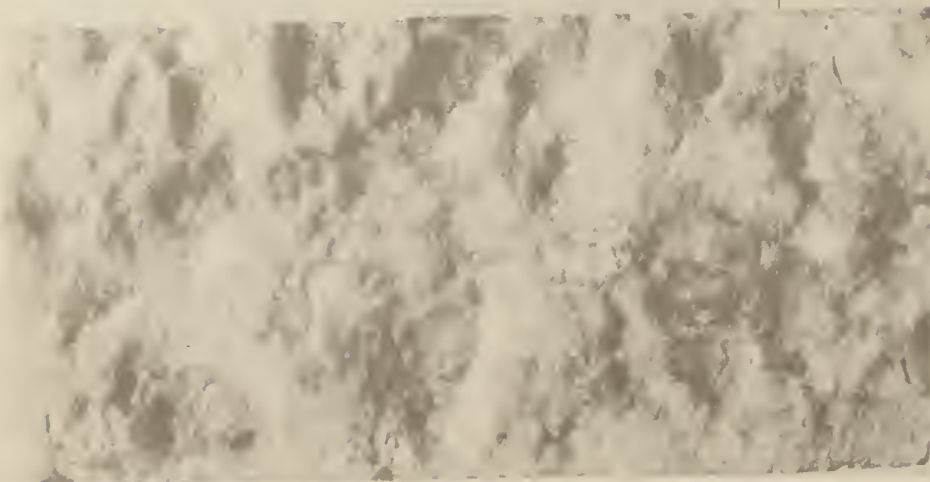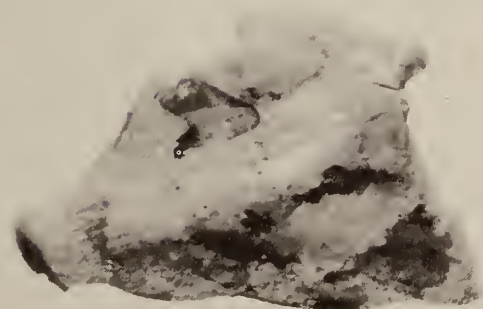
METHYL METHACRYLATE

METHYL METHACRYLATE + SILANE

Figure 3-7. Fracture surfaces of PC specimens. Top: specimens pre-
pared without silane coupling agent, tensile splitting failure occurred
at polymer-aggregate interface. Bottom: specimen prepared using
silane, failure occurred through aggregate.

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POLYMER CONCRETE

METHYL METHACRYLATE + SILANE

METHYL METHACRYLATE

AFTER EXTRACTION

Figure 3-8. Polymer-concrete specimens after contact with boiling benzene for 24 hr. Left, PC containing MMA and silane; right, PC containing MMA.

41

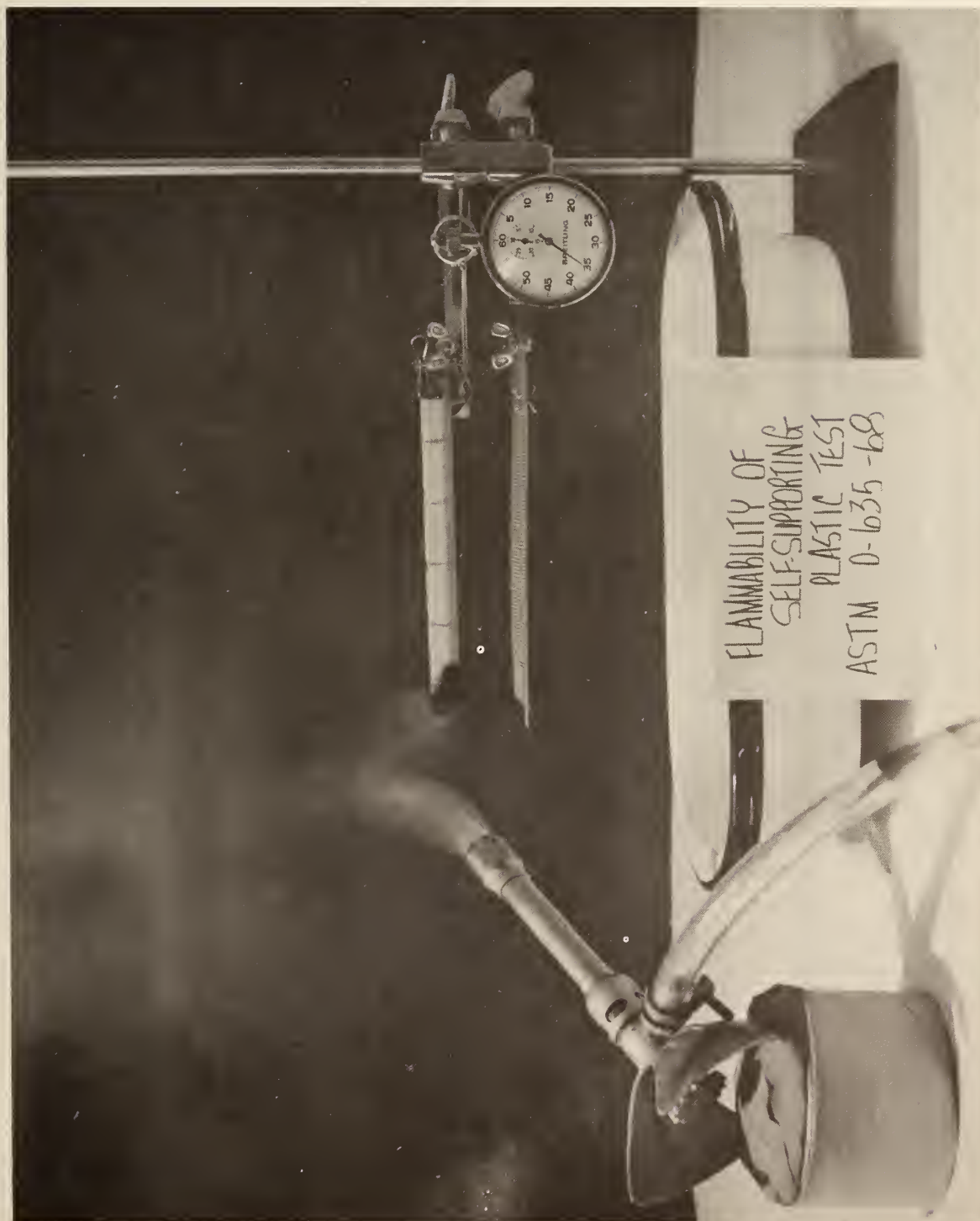Figure 3-9. Flammability test of PIC specimen containing MMA. Specimen burns while flame is applied.

42

Figure 3-10. Flammability of PIC specimen containing MMA. On removal of flame source, flame dies out almost immediately.

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Table 3-7

Determination of the Relative Flammability of Plastics,[a] Polymer-Inpregnated Concrete, and Polymer-Concrete Composites

Polymer	Composite	Polymer conc., wt %	Burning rate, in min	Remarks
Methyl methacrylate	–	100	1.2	Burning by this test
Styrene	–	100	1.0	Burning by this test
tert.-butyl styrene	–	100	0.9	Burning by this test
Chlorostyrene	–	100	0	Self-extinguishing by this test
10% Polyester – 90% styrene	–	100	0.9	Burning by this test
60% Styrene – 40% TMPTMA	–	100	0.8	Burning by this test
Methyl methacrylate	PIC	6.5	–	Self-extinguishing in 45 sec; two 30-sec ignitions
Styrene	PIC	6.3	–	Self-extinguishing in 30 sec; two 30-sec ignitions
tert.-butyl styrene	PIC	6.5	–	Does not support combustion; two ignitions
Chlorostyrene	PIC	6.2	–	Does not support combustion; two ignitions
60% Styrene – 40% TMPTMA	PIC	6.5	–	Self-extinguishing in 10 sec; two ignitions
Methyl methacrylate	PC	8.0	–	Self-extinguishing flame; travels 2 in. in 2.5 min
Styrene	PC	7.6	–	Self-extinguishing; <1 in. flame travel in 2.5 min
tert.-butyl styrene	PC	7.4	–	Does not support combustion
Chlorostyrene	PC	7.6	–	Does not support combustion
10% Polyester – 90% styrene	PC	6.9	–	Self-extinguishing; burns for 1.5 sec
60% Styrene – 40% TMPTMA	PC	7.0	–	Self-extinguishing; burns for 15 sec

[a]ASTM D 635-68, Flammability of Self-Supporting Plastics.

conditions of the test described above, polymer-impregnated concrete and polymer-concrete composites are either self-extinguishing or do not burn. The polymer on the surfaces of the composites that had been exposed to a flame was observed to burn or to pyrolize and leave a charred residue, which formed a protective blanket for polymer beneath the surface.

8. Storage and Handling of Monomers

Most monomers, including those described in this section contain inhibitors when they are shipped by the manufacturers. Inhibitors are chemical compounds that prevent premature polymerization in two ways:

(1) They can react with and deactivate the free radical in a growing chain.

(2) They can act as an antioxidant and prevent polymerization by reacting with oxidation products that may be formed in the storage vessel through contamination or through the formation of peroxides from oxygen in the air.

In general, inhibitors serve as free-radical scavengers. The inhibitor level must be maintained above a minimum concentration, or danger level, at all times. If the concentration is allowed to drop below this danger level, the amount remaining may not be adequate to prevent a premature or runaway polymerization. The danger level for styrene is ~4 to 5 ppm. Maintaining the inhibitor concentration in the 10 to 50 ppm range gives adequate control.

The time required for initial inhibitor concentrations to fall to a dangerous level varies greatly with storage and handling conditions. Factors affecting the depletion of inhibitor are heat, water, and air, with heat the most important. In hot climates (normal temperatures $>30^{\circ}$C), the bulk monomer should be cooled.

Drums of monomer should not be permitted to stand in the sun for more than a short time. As soon as possible after being received, monomer should be placed in a cool, shaded area. In hot weather, drums can be cooled by water spray. It is also advisable to keep inventories to a minimum during hot weather and use them in the order received so that monomer is not stored any longer than necessary. Table 3-8 lists the inhibtiors used by the manusfactuers of various monomers. Typical inhibitor concentrations for each monomer at time of shipping are also given. It should be noted that the inhibitor concentrations that are normally available vary widely. The concentrations given in Table 3-8 have been satisfactory for work at BNL.

Table 3-8

Commonly Used Monomer - Inhibitor Combinations

Monomer	Inhibitor	Concentration, ppm
Styrene	t-butyl pyrocathecol	45-55
Methyl Methacrylate	hydroquinone	30-40
Trimethylolpropane trimethacrylate (TMPTMA)	monomethylether of hydroquinone	200
Polyester-styrene	t-butyl pyrocathecol	10-20

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There are various chemical methods for monitoring inhibitor concentration. A fast and simple method developed at BNL is described in Chapters IV and V. Since the inhibitors are specific for a given monomer, care must be taken that any inhibitor added to the monomers is the same as that originally used by the manufacturer. All the inhibitors are commercially available; sources are given in Appendix B.

Of the monomers designated in this section for FHWA application, only methyl methacrylate is classified as a flammable liquid (because the flash point is $<27^{\circ}C$) by the Interstate Commerce Commission (ICC). Although less hazardous, the other monomers are nevertheless combustible materials and they should be treated as such.

Monomer handling areas should be well ventilated. All tanks and hose connections must be grounded for the safe discharge of static electricity, and explosion-proof motors are required. Fires involving monomers can be safely extinguished with foam, dry powder, or carbon dioxide.

If monomer has been spilled it can be rendered safe for disposal by covering it with a suitable absorbing agent, such as sand. Some absorbing agents such as untreated clays and micas will cause an exothermic reaction that might ignite the monomer.

Finally, a few words about catalysts and promoters. The catalysts used for this work are organic peroxides and should be kept in a cool place, away from heat or any source of sparks. They should be stored separately, away from monomer and in particular away from promoters or other oxidizing materials. Inventories should be kept to a minimum. Peroxide catalysts have a limited shelf life and therefore lose efficiency with time. Measurements for determining catalyst efficiency are discussed in Chapter V.

Any catalyst accidently spilled should be swept up and disposed of immediately. The spilled or waste catalyst should be mixed with an incombustible material such as vermiculite or perlite in amounts equal to that of the catalyst. The mixture should be saturated with water, the excess allowed to drain off, and the wet residual mass carefully burned in an open incinerator or shallow trench. The torch used to ignite the mass should be at least 6 ft long, and confinement should be avoided.

9. <u>Monomer Curing Precautions</u>

The preparation of monomer systems with catalysts and or promoters should be done by a person who is knowledgeable

in the use of these materials. The addition of these materials
to monomers is a critical step in the preparation of polymer-
impregnated concrete and polymer-concrete composites.
Proper procedures will minimize any hazards involved in the
use of these highly reactive materials and will also result
in controlled polymerization. Table 3-9 lists some of
the important DO'S and DONT'S in the preparation of catalyzed
monomer systems.

Table 3-9

<u>CURING PRECAUTIONS FOR MONOMERS</u>

1. <u>Never</u> mix promoters directly with peroxide catalysts

2. When promoters are used to produce a "room temperature" setting mixture:

    a) add all promoters to the resin and <u>disperse</u> <u>thoroughly</u>.

    b) add the peroxide catalyst just <u>prior</u> to use.

    c) never add promoter mixtures to catalyst mixtures

3. For a thermal-catalytic cure when promoters are not used:

    a) slowly add a <u>liquid</u> <u>catalyst</u> to the monomer and disperse thoroughly

    b) dissolve a <u>solid</u> catalyst in a small amount of monomer, add this mixture to the large batch.

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METHODS OF PRODUCING POLYMER-IMPREGNATED CONCRETE
L. E. Kukacka

Introduction

The basic method of producing polymer-impregnated concrete (PIC), shown schematically in Figure 4-1, consists of the fabrication of precast concrete specimens, oven-drying, saturation with monomer, and in situ polymerization. Processing requirements for each of these steps are being developed.

A number of concrete preparation variables, such as mix composition, method and duration of curing, and drying temperature, have been investigated to determine the effects on the properties of the composite material. Experiments have also been performed to determine the process conditions required to fully and partially impregnate various types of concrete. Variables such as degree of vacuum, evacuation time, saturation time, pressure, and monomer viscosity have been studied. The effect of concrete composition on each of these parameters has also been studied, and techniques for reducing monomer losses due to evaporation and drainage during the polymerization reaction have been evaluated. The impregnation techniques are used in conjunction with polymerization methods involving the use of radiation, chemical-initiator, and promoter-chemical initiator.

Each of these processing steps is discussed below.

1. Concrete Preparation

Composition

A considerable amount of work has been performed to determine the effects of concrete mix design variables on the properties of PIC. [4,17] In these studies, compressive strength has generally been the property evaluated. Concrete mix variables investigated include water/cement ratio, entrained air content, slump, aggregate type and quality, and the use of admixtures such as fly ash.

Data typical of those obtained by many investigators are summarized in Figure 4-2. They indicate that the impregnation of low-strength concrete (2000 psi) results in high-strength PIC (25,000 psi), essentially the same as that produced from high-strength samples (9000 psi). Concretes containing normal-weight and lightweight aggregates have also been impregnated. All the materials produced high-strength, durable composites. [17-19] Variations in the maximum aggregate size from 0.4 to 1.0 in. did not significantly affect the strength or durability of the composites. On the basis of
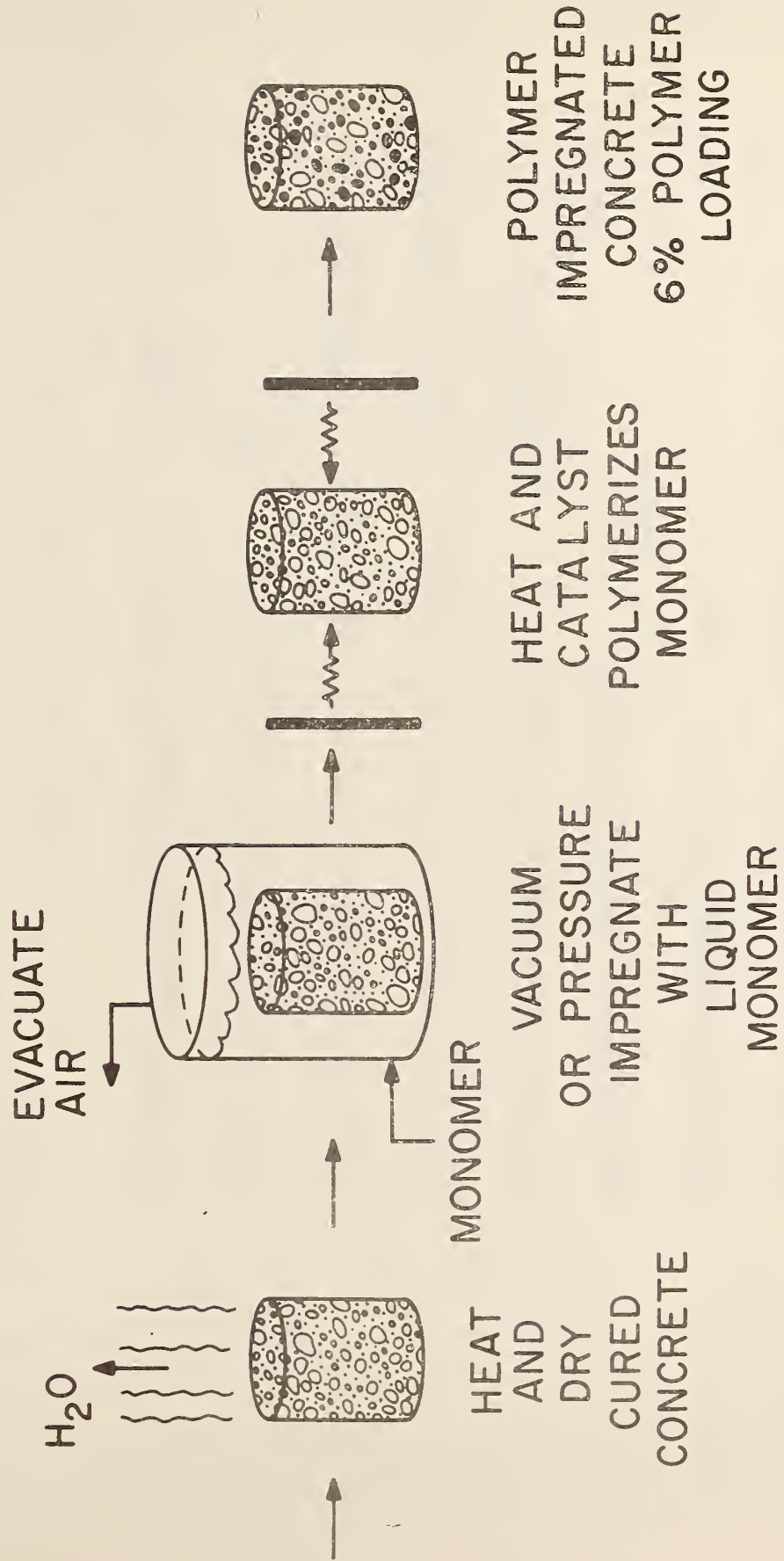
Figure 4-1. Schematic for the method of producing PIC.

POLYMER IMPREGNATED CONCRETE

PIC

EVACUATE
AIR

H_2O

MONOMER

HEAT
AND
DRY
CURED
CONCRETE

VACUUM
OR PRESSURE
IMPREGNATE
WITH
LIQUID
MONOMER

HEAT AND
CATALYST
POLYMERIZES
MONOMER

POLYMER
IMPREGNATED
CONCRETE
6% POLYMER
LOADING

LOW POROSITY
LIMESTONE
6.9 %
8.4 %
0.3 %
0.6 %

HIGH POROSITY
LIMESTONE
18.1 %
20.2 %
1.0 %
1.2 %

PIT RUN
AGGREGATE
10.0 %
11.9 %
0.3 %
0.9 %

EXPANDED SHALE
AGGREGATE
25.5 %
29.8 %
0.7 %
0.9 %

HIGH STRENGTH
≈9000 psi
6.1 %
7.1 %
0.3 %
0.3 %

LOW STRENGTH
w/c = 0.6
7.2 %
8.3 %
0.3 %
0.5 %

HIGH-ENTRAINED
AIR ≈ 10 %
9.5 %
10.0 %
0.5 %
0.5 %

LOW-ENTRAINED
AIR ≈ 2 %
5.9 %
7.2 %
0.4 %
0.5 %

COMPRESSIVE STRENGTH, psi

0   4   8   12   16   20   24   28   32

FOG CURED

HIGH-PRESSURE-STEAM CURED

MONOMER, MMA
RADIATION-INDUCED
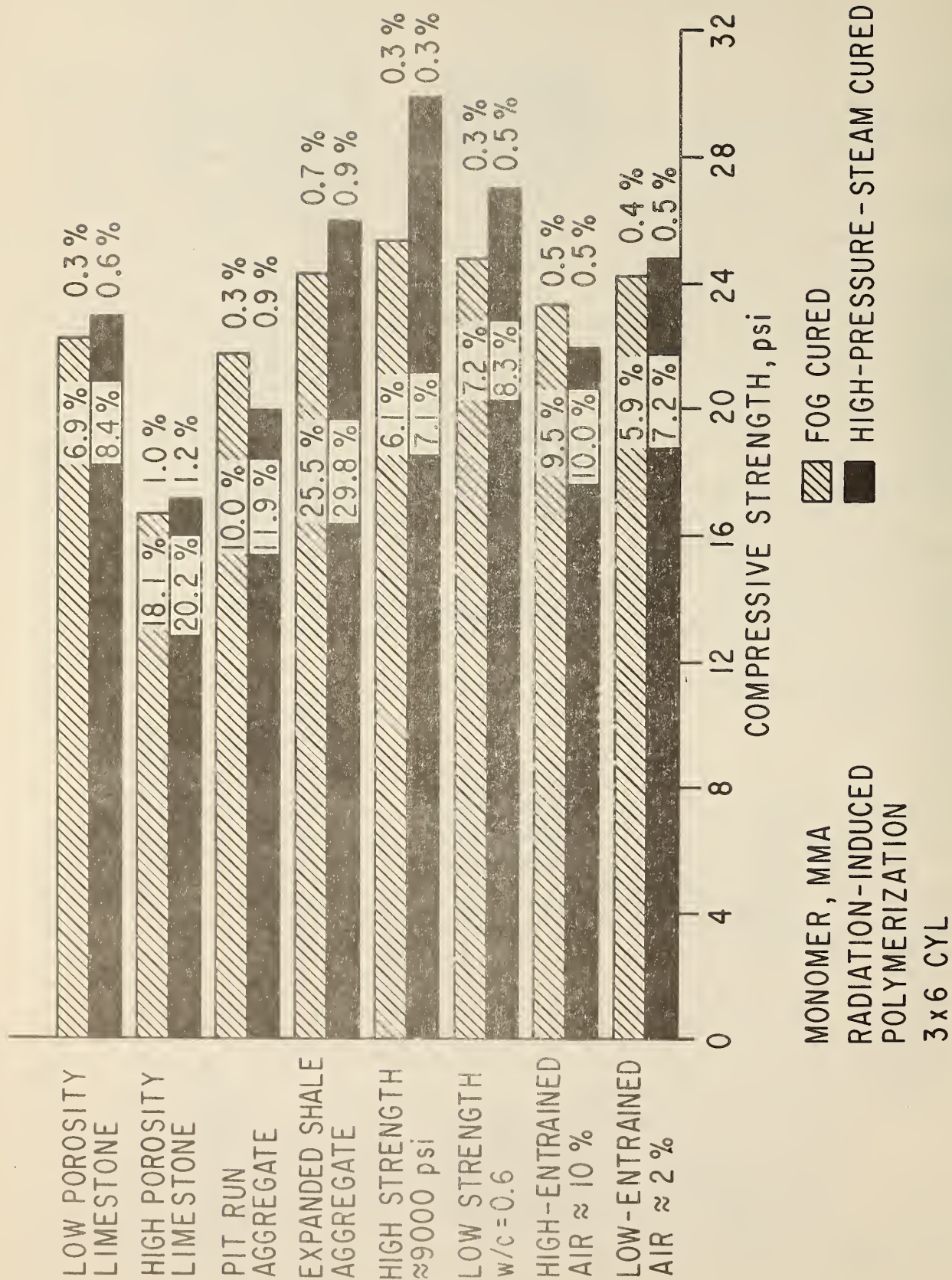POLYMERIZATION
3 x 6 CYL

Figure 4-2. Comparison of the effects of concrete mix variables and method of curing on the compressive strength of PIC.

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these results it would seem that concretes prepared from locally available materials can be used in the production of high-quality PIC.

Method and Duration of Curing

Three curing conditions, fog curing, low-pressure steam curing (LPS), and high-pressure steam curing (HPS), have been studied to determine their effects on MMA-impregnated concrete.[3,4,18] These data, some of which are summarized in Figure 4-2, indicate that HPS results in higher polymer loadings and generally higher strengths than those of comparable fog-cured specimens.

Tests to determine the effect of moist curing time[3,18] indicate that, for times varying between 2 and 28 days, the duration of moist curing does not significantly affect the final strength of PIC. These data are summarized in Figure 4-3.

Age at Impregnation

A very limited amount of work has been performed to determine the effect of concrete age at impregnation on the strength properties of PIC. Specimens impregnated 1, 28 and 63 days after completion of a 28-day cure and tested at a total age of 120 days exhibited little change in compressive and tensile strengths with age.[3]

2. Drying Requirements

The strength and durability properties of PIC are strongly affected by the fraction of the porosity of the cement phase which is filled with polymer. If maximum improvements are desired, it is necessary to dry and evacuate the precast specimens prior to impregnation. Drying temperatures up to 250°C have been evaluated.[3,18] Initial work[3] indicated that specimens dried at temperatures from 150° to 250°C, and subsequently impregnated with MMA, exhibited a slight decrease in compressive strength with increased drying temperature. Recent work[5] indicates that a drying temperature of 110°C is not high enough to remove all the water unless drying times are excessively long.

Based on experience at BNL, a drying temperature of 150°C is recommended. At this temperature the drying rates are reasonably fast (~24 hr for a 3-ft-i.d. x 6-ft-long x 4-in.-wall pipe), and a high-quality product is produced.

3. Monomer Saturation Techniques

Full Impregnation

Experiments to determine the conditions required to fully impregnate concrete have shown that process parameters such as degree of dryness and vacuum, soak pressure, and soak time all have an effect on the strength of PIC.[5,20]
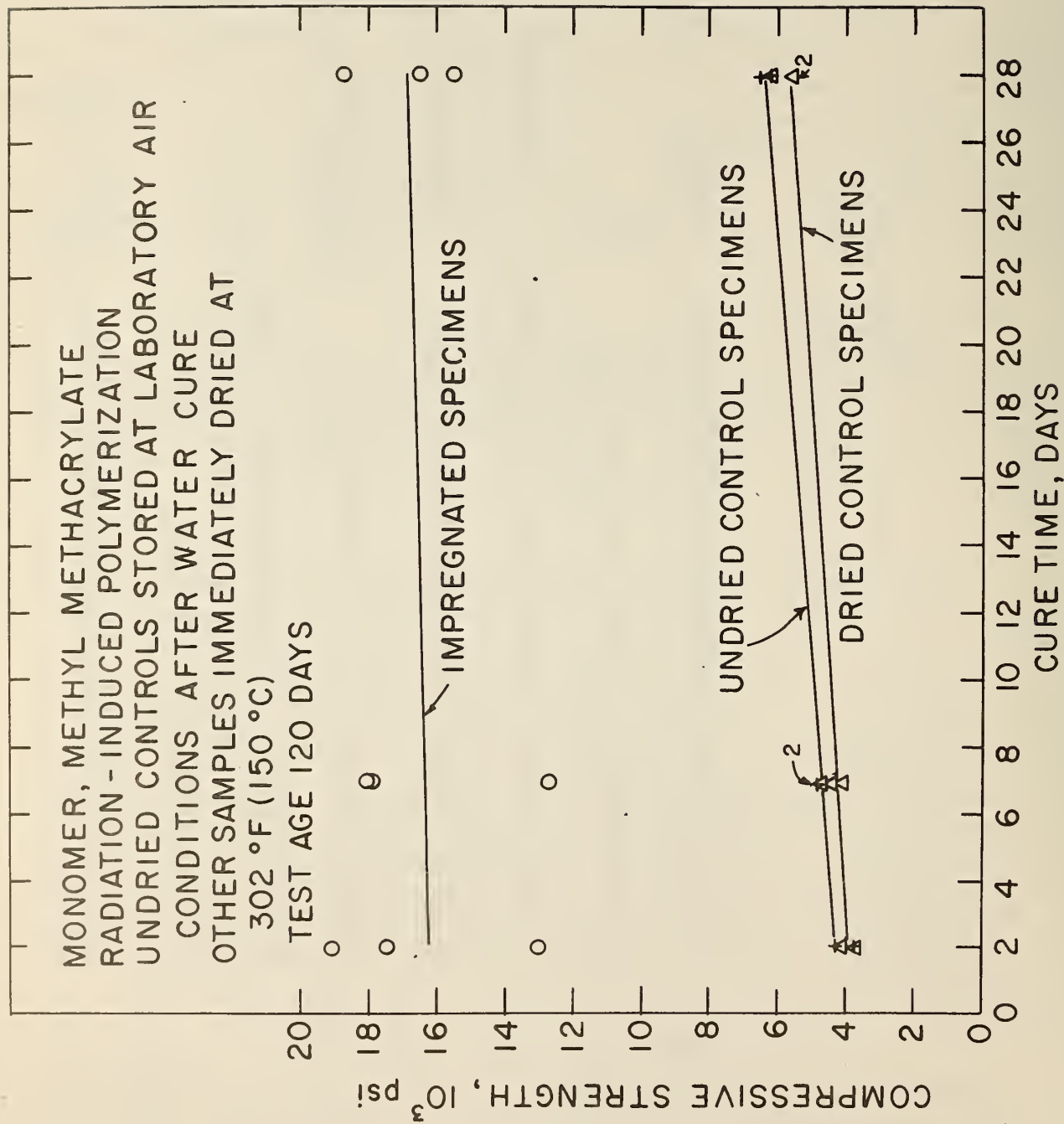
COMPRESSIVE STRENGTH vs CONCRETE CURE TIME

Figure 4-3

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Filling-rate measurements were made for CP* concrete under various impregnation conditions, (see Figure 4-4). Without prior vacuum but with the use of 100 psig pressure, the monomer loading approached equilibrium (polymer loading, 6.2 wt %) after about 10 minutes. At 10 psig, equilibrium was not achieved after 1000 minutes. The data also indicate that holding a sample at 30 in. Hg vacuum for 15 minutes and then soaking at 10 psig for 30 minutes was adequate to reach saturation. At 100 psig, saturation was achieved in considerably less time ($\approx$9 minutes).

Concrete composition significantly affects the monomer filling rate. Samples of concrete with high air and high water contents were saturated in shorter periods tnan CP concrete. The initial filling rate of the high air concrete was significantly higher than that of any of the other concretes tested. The data shown in Figure 4-5 are for specimens having identical impregnation and polymerization conditions, 30 in. Hg vacuum and 10 psig soak pressure. The plots have been normalized for the different saturation levels measured for each type of concrete by comparing elapsed time with percent of maximum monomer loading. On the basis of these data, it would appear that the filling rates are directly related to the cement phase porosity. In the case of the shale aggregate, long filling times were required, probably because of the large number of pores present in the aggregate.

The effect of monomer viscosity on the filling rate of three concrete mixes was also measured.[5,20] Pre-polymer solutions were prepared by dissolving PMMA in MMA until viscosities of 20 and 70 cP were measured. These data, shown in Figure 4-6 were compared with filling data using normal MMA (0.7 cP) under impregnation conditions of 30 in. Hg vacuum and 10 psig. Specimens of concrete with a high water-to-cement ratio were fully impregnated with the higher viscosity monomer solutions in 1000 minutes. After polymerization, all the specimens had similar compresssive strengths.

The simplest type of impregnation process would consist of soaking unevacuated samples at atmospheric pressure. This would result in partially saturated specimens and therefore somewhat lower strengths. In general, overnight soaking of dried CP-type concrete in MMA will result in filling ~70 to 80% of the voids that can be filled by prior evacuation. Compressive strengths in the range of 15,000 to 17,000 psi would be anticipated.

Partial Impregnation
Partially impregnated concrete is designed for durability rather than high strength, which permits a saving in the amount of monomer as compared with fully impregnated concrete. The concrete

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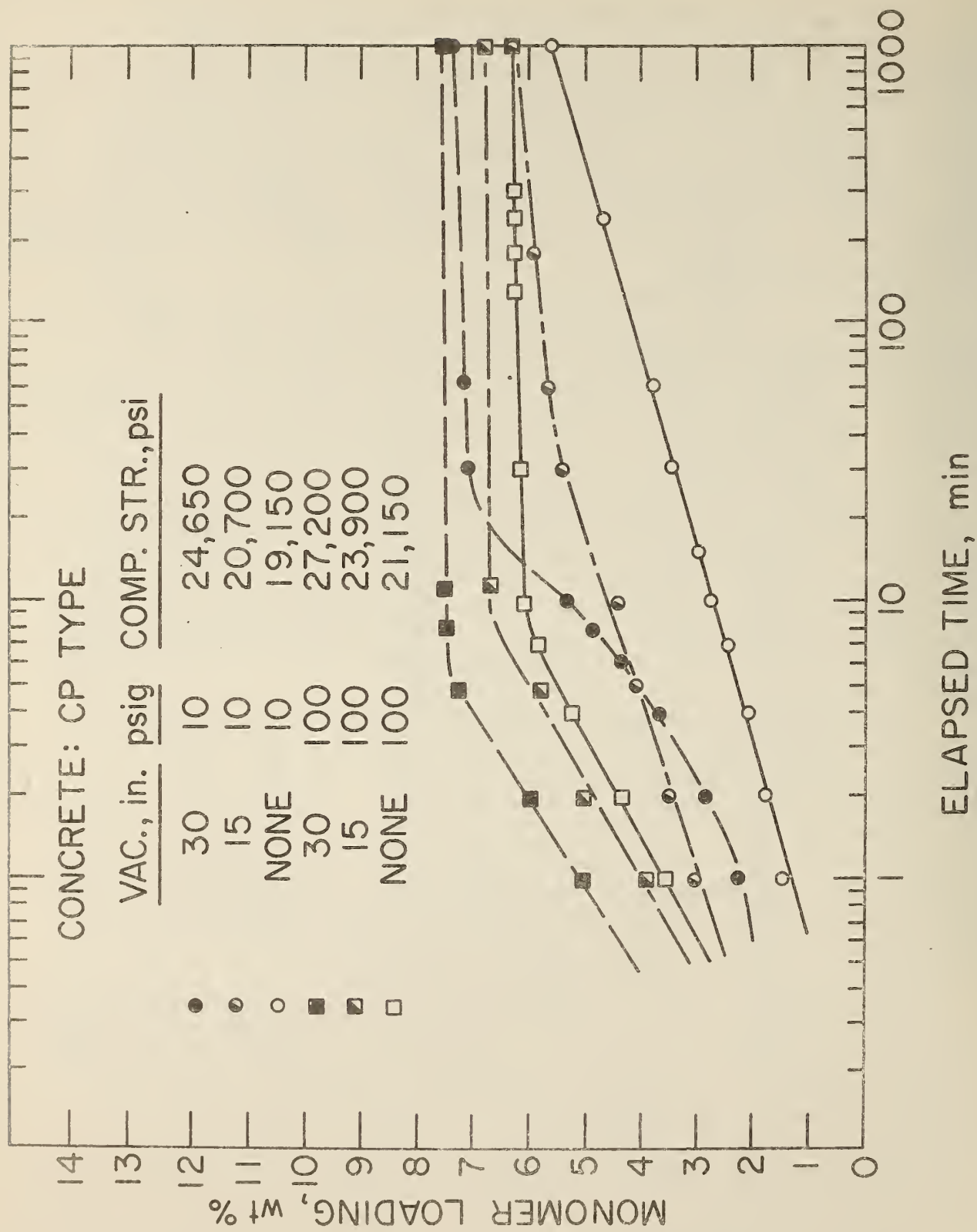*Standard concrete mix used at USBR in concrete-polymer program. See Ref. 1.

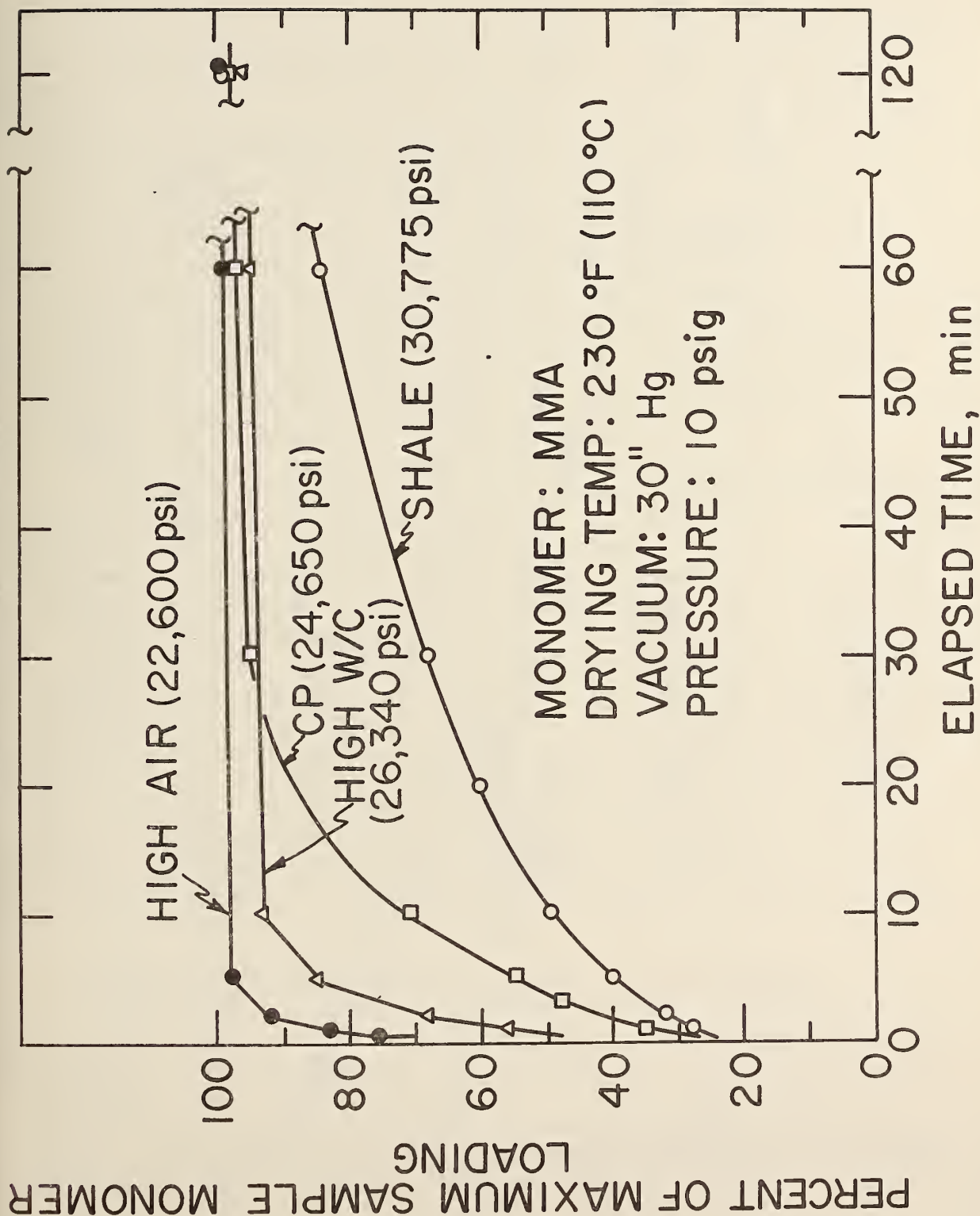Figure 4-4. The effect of vacuum and pressure on impregnation of CP-type concrete previously dried at 110°C.

Figure 4-5. Comparison of impregnation rates and compressive strength measurements for various concretes.
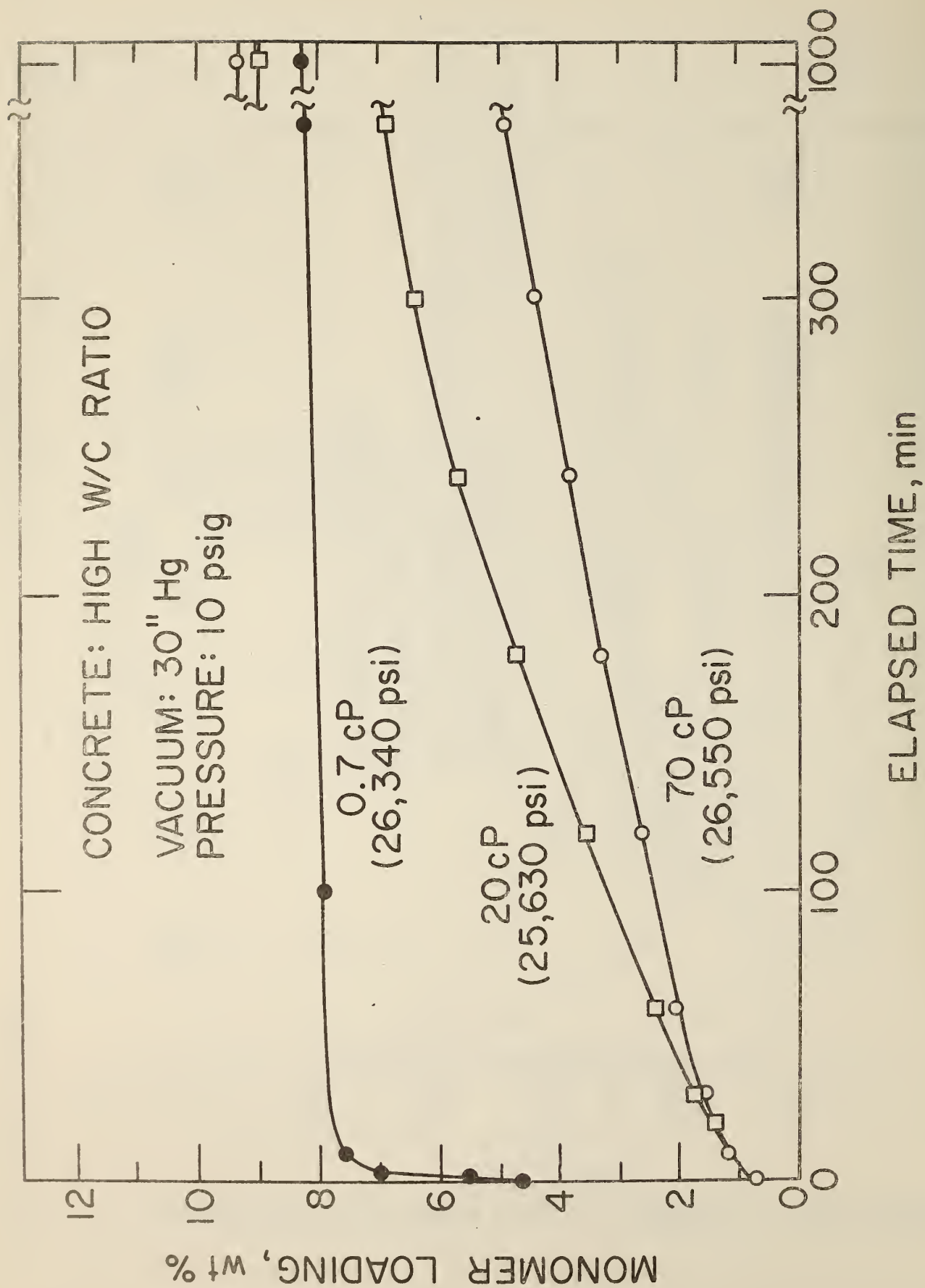
Figure 4-6. Effect of monomer vicosity on the impregnation rate and final compressive strength of concrete.

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is impregnated to controlled depths of penetration. The monomers should effectively seal the surface and penetrate to a sufficient depth to avoid separation of the impregnated layer and premature failure. Viscous monomer systems are generally used because penetration depths are more easily controlled, voids in the penetrated portion remain filled, and monomer losses due to evaporation and drainage during the time between impregnation and complete polymerization are lower. However, for field applications such as the repair of concrete-lined vessels and bridge decks, low viscosity monomers such as MMA, MMA-TMPTMA, and styrene-TMTPMA are preferred, since they require less severe impregnation conditions.

Techniques for the partial impregnation of concrete have been published.[3,4,21] Two processes, treatment of all surfaces and of one surface, have been described. The former (see Figure 4-7) can be accomplished by soaking in low viscosity monomers. In work of this type, dried 4-in. cubes made from 5600 psi control concrete were soaked in monomer for periods varying from 5 min to 48 hr. Over this period the polymer loading and depth of penetration showed a nearly linear relationship with log soak time.[18]

The use of higher viscosity monomers results in a more uniform depth of penetration and greater control.[4,21] With these materials, positive pressures are required. A soak time of ~5 hr at 100 psig was required to obtain a 3/4-in. penetration with a 67.5 wt % styrene - 32.5 wt % polyester mixture. (viscosity, 10 cP). A typical sample is shown in Figure 4-8.

Surface treatments of up to 1 in. deep from one side have been achieved on bridge decks.[22] Simple ponding of MMA resulted in penetration to a depth of 1/4 in. in the concrete. By placing a thin layer (~1/4 in.) of dried fine aggregate over the surface, greater depths of penetration have been achieved (up to 2 in.). The aggregate is reported to act as a wick for the monomer, and thus longer soak periods (up to 25 hr) are possible without excessive evaporation. It was found that soak times >10 hr produced a substantial polymer surface treatment. This method was recently used by the USBR to impregnate to a depth of ~1.5 in.

4. Encapsulation Techniques to Reduce Monomer Losses

Care must be taken to minimize monomer evaporation and drainage losses from the concrete during the polymerization reaction. Evaporation is a problem when high vapor pressure monomers such as MMA are used. A specimen that exhibited excessive loss of monomer due to evaporation is shown in Figure 4-9. Monomer drainage losses become appreciable when low-density concretes are impregnated.
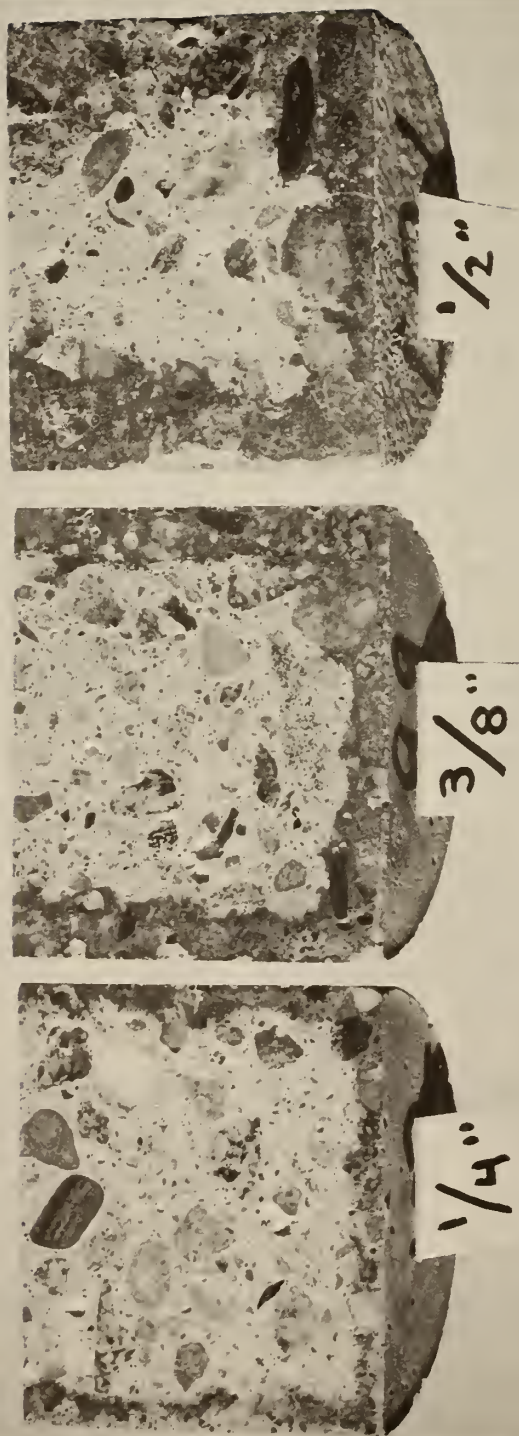
Figure 4-7. Cross sections of CP-type concrete sections partially impregnated with polyester-styrene.
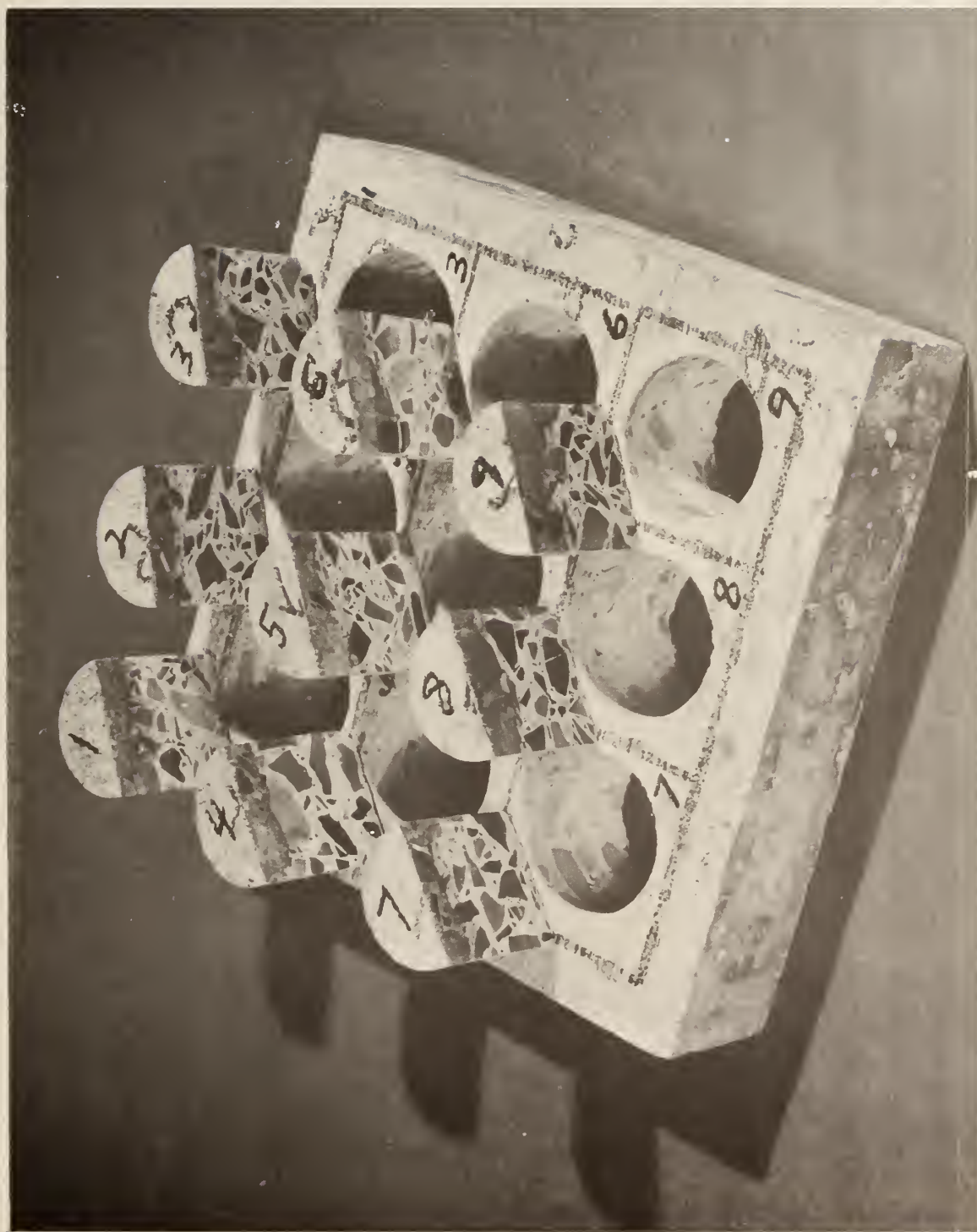
Figure 4-8. Cross sections of core samples taken from a highway-quality concrete slab partially impregnated with 67.5 wt % styrene - 32.5 wt % polyester on one surface to a depth of 3/4 inch.

Figure 4-9. Surface depletion of MMA from cut sections of PIC.

The following methods for reducing these losses have been investigated.[4,17,18,20-23]

1. Wrapping of monomer-saturated specimens in polyethylene sheet or aluminum foil.

2. Encapsulation of the specimen in a form during impregnation and polymerization.

3. Polymerization with the monomer-saturated specimens in contact with water.

4. Impregnation with monomer followed by a pre-polymer dip, wrapping, and rotation during polymerization.

Of the methods studied, underwater polymerization appears to be the most practical for large-scale application. Pipe, beams, and prototype bridge-deck panels have been treated in this manner. The method has been used successfully in conjunction with radiation and thermal-catalytic polymerization.[5] If the water is saturated with monomer prior to use, very little surface depletion is observed. The results [17,18,21] also indicate that underwater polymerization has no detrimental effects on the properties and can produce specimens with highly reproducible polymer loadings.

It should be noted that the underwater method for the radiation and thermal-catalytic process results in the formation of polymer in the water. When drained, the polymer may adhere to the walls of the impregnator and collect in valves and piping. This problem is essentially one of design and is caused primarily by the polymerization of nondrainable monomer. Less polymer is formed in the thermal-catalytic process, probably because of the decreased solubility of MMA in water at the elevated temperature. The problem can be minimized by proper design and is more than compensated for by the reduced evaporation and drainage losses.

5. Polymerization Techniques

There are three general methods for the bulk polymerization of monomers currently being used in PIC. These are radiation, thermal-catalytic, and promoter-catalyst. Although the same methods are applicable to the in situ polymerization of monomers in concrete, each process must be fully evaluated to take into account the effects of drainage and evaporation losses from the concrete during the polymerization, the safety problems associated with the storage and reuse of large quantities of monomer and catalyst, and the economics of the entire process.

Radiation-Induced Polymerization

The radiation-induced polymerization of monomers in concrete has been performed in air and under water.[1-3,5,19] The principal advantage of the process is the elimination of a catalyst, which allows essentially unlimited storage and reuse of monomer. In addition, polymerization can be initiated at room temperature and at a uniform rate within relatively thick concrete sections. Detrimental features include the high cost of radiation sources, the necessity of massive biological shielding, and the low polymerization rates. The latter, when combined with the radiation attenuation due to the thick sections and high density, results in large radiation requirements and long processing times.

Thermal-Catalytic Polymerization

The polymerization method involving the use of chemical initiators and heat, commonly referred to as the thermal-catalytic process, has been used extensively for preparing PIC and appears the most practical for present-day use. The process can be performed in air or under water. Several catalysts that have been used in this work are described in Chapter V.

The primary advantage of the thermal-catalytic polymerization method is that the polymerization rates are very rapid and therefore processing times are short. Relatively simple electric ovens, water, or raw steam can be used as a heat source.[5,17,18,22,23] A disadvantage is that the chemical initiator must be dissolved in the monomer prior to introducing the mixture into the concrete. In a commerical operation of almost any size this will involve storing and handling of large batches of monomer containing chemical initiator. Although potentially dangerous, the use of relatively stable azo-type initiators in conjunction with established safety codes can reduce the hazards to manageable levels.[4,5] Catalyzed monomers have been safely stored at BNL and the USBR for periods >1 yr.

Promoter-Catalyst Polymerization

The primary advantage of a promoter-catalyst system is that polymerization can be initiated at ambient temperature without the need for an external source of energy. Disadvantages are the difficulties in obtaining predictable

polymerization times and in matching the monomer saturation time with that of the onset of polymerization.

The techniques for using promoter-catalyst systems to produce PIC have not yet been demonstrated on a large scale. However, the system is being used in field applications. [5,17,22,24,25] In all the work the materials were mixed immediately before application. Methods of application include injection, spraying, paint brushes, and rollers. A list of the promoters currently being used is given in Chapter V.

6. Monomer Handling Techniques

The handling of monomers, particularly in large volumes, requires rigid safety controls. Monomers when shipped from the manufacturers contain sufficient inhibitor to maintain safety during shipping and storage. Manufacturers recommend proper storage temperatures, toxicity limits, and other precautions pertinent to safe handling of the monomers.

A decrease in inhibitor concentration with time or contact with concrete indicates that the monomer is becoming unstable and may ultimately polymerize. Therefore the monomer must be tested periodically to determine the inhibitor concentration. Inhibitor concentrations can be measured by various chemical and colorimetric methods, but after the monomers have come in contact with concrete, these methods may not give satisfactory results. A peak exotherm method has been used successfully to determine the inhibitor concentration of monomers after contact with concrete. [2] This method consists of adding a measured amount of catalyst to a known volume of monomer and placing the mixture in a temperature bath. The time required for the mixture to reach a point at which the polymerization reaction produces a maximum temperature is recorded and compared with a previously prepared calibration curve for the mixture. A typical calibration curve for the MMA-benzoyl peroxide-hydroquinone system is given in Ref. 2. Excellent reproducibility was obtained when monomer volume, tube size, initiation temperature, and catalyst concentration were kept constant.

The greatest potential hazards exist when a catalyst has been added to the monomer, as in the thermal-catalytic processing method. In this case the catalyst concentration is well in excess of the inhibitor concentration and rapid premature polymerization could occur under unfavorable conditions. Catalyst concentration can also be measured by the peak exotherm method, in which the inhibitor concentration is held constant and that of the catalyst is varied. However, the method is less reliable for determining catalyst concentration than for determining inhibitor concentration.

Many monomers have low flash points and are therefore Class I flammable liquids, as defined by the National Fire Protection Association. Precaution should therefore be taken to prevent exposure to flames, sparks, or other ignition sources. All containers should be electrically grounded. Electrical devices in areas where monomers are handled should be explosion proof, and spark proof tools should be used.

Bulk storage vessels should be vented, and all vents should be protected with flame arresters. Such vessels should also be provided with rupture disks properly sized so that in the event of bulk polymerization within the vessel, the fluid can be vented rapidly and the buildup of excessive pressure prevented.

7. Recommendations

High-quality PIC can be made from concretes with a wide variety of compositions. For best results, the use of standard-weight concretes containing a good-quality aggregate is recommended. With this type of concrete, high-pressure steam curing appears to be advantageous.

For a high-pressure steam-cured, standard-weight concrete containing a low-porosity aggregate, the following processing cycle is recommended for sections up to 12 in. thick.

1. Oven-dry to constant weight at 150°C. Dryness should be achieved in 24 hr.

2. Evacuate section to 30 in. Hg and maintain for 30 min.

3. Introduce monomer under vacuum and subsequently pressurize to 10 psig. Pressure-soak for 60 min.

4. Remove monomer.

5. Remove and place section in water or, for larger sections, back-fill impregnator with water.

6. Polymerize monomer *in situ* with hot water.

7. Remove water and clean section.

CHAPTER V

TECHNIQUES FOR THE PREPARATION OF POLYMER-CONCRETE

J. Fontana

Polymer-concrete (PC) consists of an aggregate mixed with a monomer which is subsequently polymerized in place. The techniques used for mixing and placement are similar to those used for portland cement concrete, and after curing a high-strength, durable material is produced. Process variables studied include monomer type, aggregate size distribution, and polymerization method. Other topics discussed in this chapter include placement and finishing techniques, the effects of additives such as coupling agents, and safety requirements for mixing and placement.

1. Polymer-Concrete Fabrication Techniques

Monomer Selection

The important considerations in the selection of a monomer system for use in PC include cost, durability under anticipated exposure conditions, adhesion to aggregate, and ideally the ability to be polymerized at ambient temperature by promoter-catalyst techniques in a highly predictable manner. Low vapor pressure is also an important characteristic, since it results in reduced evaporation losses and minimizes safety problems.

Two monomer systems that have been studied extensively at BNL are methyl methacrylate (MMA) and polyester-styrene. It is expensive to polymerize MMA alone in a predictable manner with use of promoter-catalyst techniques, but, with this exception, both materials in general meet the selection criteria listed above. The polymerization problem can be overcome by the addition of a polyfunctional monomer such as trimethylolpropane trimethacrylate (TMPTMA) to the MMA. This results in a greatly enhanced polymerization rate and produces a cross-linked polymer with increased temperature and solvent resistance. Based on this finding, two monomer systems, 95 wt % MMA-5 wt % TMPTMA and 54 wt % polyester-46 wt % styrene are currently being used in laboratory and field tests. Polymerization conditions for these systems and several other monomer mixtures are summarized in Table 5-1.

Mix Design

The design of a mix to optimize the properties of PC is largely accomplished by aggregate gradation to give a void volume that will require minimal amounts of monomer to fill

Table 5-1

Promoter-Catalyst Systems For Monomer Mixtures

Monomer mixture	Viscosity at 77°F (25°C) cP	Catalyst	Concentration, wt %	Promoter	Concentration, wt %	Ambient temperature, °F	Ambient temperature, °C	Gel time, min	Cure time, min
MMA	0.5	Bzp + AIBN	0.5/0.5	DMA + DMT	0.5/0.5	77	25	20	60
95% MMA – 5% TMPTMA	~1.0	Bzp + AIBN	1.0/1.0	DMA + DMT	1.0/1.0	77	25	15	36
95% MMA – 5% TMPTMA	~1.0	Bzp	2.0	DMA	2.0	82	28	20	38
70% MMA – 30% TMPTMA	1.9	Bzp	1.0	DMT	1.0	77	25	8	14
90% styrene – 10% TMPTMA	~1.0	Bzp	1.0	DMA	1.0	106	88	-	-
90% styrene – 10% TMPTMA	~1.0	Bzp	2.0	DMA	2.0	106	88	50	1050
85% styrene – 15% TMPTMA	~1.2	Bzp	2.0	DMA	1.0	106	88	30	220
60% styrene – 40% TMPTMA	1.7	Bzp	1.0	DMA + DMT	0.5/0.5	77	25	15	45
75% styrene – 25% polyester	2.4	MEKP	1.0	CoN	0.4	60	16	53	< 120
54% polyester – 46% styrene	~100	MEKP	0.75	CoN	0.75	70	21	20	35

Bzp, benzoyl peroxide

AIBN, azobisisobutyronitrile

CoN, cobalt naphthenate

DMA, dimethyl aniline

DMT, dimethyl toluidine

MEKP, methylethyl ketone peroxide

the voids and to give good workability to the mix. This work has been described by many authors.[4,5,26,29] In general, the aggregate should be dried prior to use. Some epoxy resins are less affected by moisture and therefore the drying conditions are less stringent. The major mix variables are maximum particle size, gradation, and composition. Crushed stone and natural sand and gravel are generally used. Finely divided materials such as portland cement, powdered chalk, fly ash, and silica have also been used. Test results indicate that aggregate type and composition do not significantly influence the strength properties of the mix[29] but do affect the durability.[30] Aggregate gradation and maximum particle size influence the amount of resin required to coat the filler particles and to fill the voids. Tests have indicated that for a well-graded filler, larger maximum particle sizes require less resin. Gap grading also tends to reduce the amount of resin required. Conversely, smaller maximum particle sizes produce higher strength mixes. An aggregate size distribution has been developed at USBR[5] which, when mixed with 7 to 8% MMA produces specimens with compressive strengths of ~19,000 psi. Work at BNL has indicated that dense graded aggregate mixes of the type used in asphaltic concrete (see Table 5-2) will produce composites with a strength of 13,000 psi when mixed with 9% of a MMA-TMPTMA monomer system.[25]

The monomer content of the mix, a dependent variable, is the minimum necessary to coat the aggregate and to fill the voids. Excess monomer will bleed to the surface because of the low density relative to the density of the aggregate. Monomer concentrations ranging from 5 to 30 wt % have been reported. The former was obtained in pipe when a compaction method involving pressure, vibration, and centrifugal force was used in conjunction with a graded aggregate and filler.[30]

Fabrication Methods

The batching, mixing, and placing techniques for producing PC are largely based on adaptation of existing equipment and methods for producing portland cement concrete. However, volatile and potentially explosive monomers, such as MMA, require nonsparking and explosion-proof equipment. Mixing should be done in a closed system or outdoors in a well-ventilated area. Some of the chemicals may be irritants or toxic and should be handled in accordance with recognized safe practices.

Table 5-2

Sieve Analysis for Aggregate Used in Polymer Concrete

Sieve size	Quantity passing through sieve, %
3/4 in.	94.8
1/2 in.	83.1
3/8 in.	78.1
1/4 in.	61.6
No. 4	51.8
No. 8	40.9
No. 16	37.1
No. 30	30.5
No. 50	11.0
No. 100	2.6
No. 200	1.2

The PC mix is cast into forms or molds in a manner similar to that for conventional concrete. Wood, steel, glass, and paper molds have all been used successfully. A great variety of mold-releasing agents, such as silicone gels, vegetable oils, automobile wax, and paraffins, have also been used.

After placing, the mix should be consolidated by external vibration, rodding, mechanical pressure, or application of vacuum to remove entrapped air. The MMA-TMPTMA composite cannot be vibrated by using finger vibrators such as those used for concrete. Tamping with a concrete tamper works well·and the surface can be screeded. If the largest aggregate size used is 3/8 to 1/2 in., the screeding gives a good even surface that appears to be skid resistant. If the aggregate is 3/4 in. or larger, the screeding tends to pull the stones to the surface and causes an uneven and very rough surface. With the larger stone, tamping seems to give a better surface finish.

The polyester-styrene composites can be vibrated since the material is a sticky mass and will not separate like the MMA-TMPTMA composites. The composite closely resembles concrete in its workability characteristics, therefore it can be screeded as well as troweled.

Polymerization Techniques

Two polymerization methods are generally used to produce PC composites. One method, commonly referred to as the thermal-catalytic process, requires the addition of a catalyst, usually in the form of an organic peroxide, to the monomer. When the mixture is heated to the decomposition temperature of the catalyst, the polymerization reaction starts. The decomposition temperature varies with the type of peroxide used. In general, the polymerization rate increases with increased catalyst concentration and temperature.

The promoter-catalytic polymerization method is generally used for field applications, since the reaction can be initiated at ambient temperature.

Promoters, or accelerators, are compounds that decompose peroxide catalysts at temperatures below the critical temperature of the peroxide. Promoters must be selected with care, since each one is usually most effective with a specific peroxide catalyst. When promoters are used to produce a room-temperature setting mixture, the catalyst should be added to the monomer as the last step just prior to the use. The activity of the promoter can be attributed to its reactivity with the catalyst, as evidenced by the fact that if the two are mixed accidentally, an explosive reaction will ensue.

The polymerization reaction is exothermic and therefore a temperature rise occurs. The amount of heat liberated is dependent upon the catalyst-promoter system selected. The rate at which heat is formed and the maximum temperature reached are dependent upon volume, shape, ambient temperature, aggregate, and the catalyst system. The exotherm temperature should be ~90°C or higher to ensure a complete cure of the monomer.

The MMA-TMPTMA system has been widely used in laboratory and field experiments. The promoters used are dimethyl aniline (DMA) and dimethyl-toluidine (DMT), and benzoyl peroxide is the catalyst. If the ambient temperature is ~24°C, a concentration of 1.5% DMA and 1.5% catalyst will give a gel time of ~20 min and a cure time of 45 min. If the ambient temperature is lower, 0.5 to 1% of DMT is added to the DMA. At a temperature of 7°C, this system will set up in ~20 min and cure in <1 hr. Polymerization conditions are listed in Appendix A.

The following PC formulation has been used extensively in the field: 12 to 15% monomer (95% MMA - 5% TMPTMA) by weight of aggregate, 1% DMA by weight of monomer, 0.5% DMT by weight of monomer, and 1.5% benzoyl peroxide by weight of monomer.

The promoter and catalyst concentrations are adjusted in the field at the time of the pour to reflect changes in ambient conditions. After completing the pour, a black polyethylene sheet is placed over the finished surface to absorb solar energy and also to minimize evaporation losses.

The promoter-catalyst system normally used to polymerize polyester-styrene is 0.5 to 1% methyl ethyl ketone peroxide (MEKP) and 0.75 to 1% cobalt naphthenate. This mixture gels in 15 to 20 min and cures in <1 hr. Since the polyester-styrene ratios can be varied, the promoter-catalyst must be adjusted to reflect any changes in styrene concentration as well as in ambient temperature conditions. If it is desired to increase the rate of polymerization, an addition of 0.25 to 0.5% DMA will reduce the gel time to ~5 min and the cure time to ~30 min.

Additives

Additives have been mixed with the monomers to modify the properties of the composite. One such material was a silane coupling agent, used to form a chemical bond between the polymer and the aggregate. In the presence of moisture, the

silane hydrolyzes to form a silanol. The silanol has a strong affinity for silica and immediately reacts with it in an aggregate mix to form a chemical bond. The organic portion of the molecule is grafted onto the silicone atom and, on addition of a suitable monomer such as MMA, results in the formation of a chemical bond between the portion of the coupling agent and the growing polymer chain. The covalent bond between the inorganic and organic substrates produces significant changes in the chemical and physical properties of the composite.

Three of several methods that have been used for applying silane coupling agents to PC composites are shown in Figure 5-1. One method consists of adding a coupling agent directly to the monomer prior to contact with the aggregate. Another method is to wash the aggregate with an aqueous solution of a silane coupling agent. The aggregate must be dried after washing before it can be contacted with monomer.

The third method consists of exposing the aggregate to silane vapors before contacting the aggregate with monomer. The amount of silane coupling agent required to obtain a maximum degree of loading can be calculated on the basis of the total aggregate surface area. Compressive strengths obtain for PC specimens prepared by each of the described methods are shown in Figure 5-1. As noted, the strengths are higher than those obtained without the use of coupling agents. The highest strengths were obtained by using the vapor deposition method.

PC samples were made with use of a monomer mixture of 60 wt % styrene and 40 wt % TMPTMA. The effects of a silane coupling agent on the compressive strength of 3-in.-diam x 6-in.-long cylinders at 21, 121, and 143°C were compared. The silane was added to the monomer prior to its being mixed with the aggregate. At 21°C, the specimens containing silane had an average compressive strength of 12,300 psi compared with 6300 psi for specimens without silane. This ~2:1 strength ratio was maintained at all test temperatures (see Figure 5-2). In all cases, the concentration of silane was 1% of the total monomer used.

As described earlier, the role of the silane coupling agent is to form a covalent bond between the silica and the polymer. The effectiveness of this reaction was confirmed by solvent extraction methods. PC specimens containing PMMA with and without silane were exposed to boiling benzene for 24 hr. The PMMA in the composite without the silane completely dissolved, while the sample with the silane remained intact.

EFFECT OF METHOD OF SILANE COUPLING APPLICATION ON
COMPRESSIVE STRENGTH OF POLYMER-CONCRETE

Sample No.	Compressive strength psi	Method of silanization
1	13,875	1% by weight of silane blended with MMA prior to contact with aggregate and sand[a]
2	13,790	
3	13,800	
4	15,750	Aggregate and sand were treated with 1% silane hydrolyzed in water, dried, and contacted with MMA
5	15,825	
6	15,790	
7	15,900	Aggregate and sand were exposed to silane vapor before contact with MMA
8	16,150	
9	16,000	
10	11,200	No silane coupling agent added
11	10,950	
12	10,750	

[a] Union Carbide A-174 γ-methacryloxypropyltrimethoxysilane.
MMA = methyl methacrylate.

Figure 5-1

Polymer-Concrete

Effects of Silane Coupling Agent on Compressive Strength

Specimens, 3-in.-diam × 6-in.-long cylinders
Monomer, 60 wt % styrene – 40 wt % TMPTMA
Average polymer loading, 6.4 wt %

Specimen No.	Silane con-centration, %	Test temper-ature, °C	Compressive strength, psi
206	1	21	12,500
208	1	21	12,100
209	1	121	9,520
228	1	121	9,880
231	1	143	8,670
232	1	143	8,840
234	0	21	6,420
238	0	21	6,200
235	0	121	5,260
240	0	121	4,670
242	0	143	3,650
246	0	143	4,090

Aggregate Size Distribution

Mesh size	Concentration, wt %
170–270	6.1
40– 60	10.2
20– 30	23.0
0.5-in. stone	60.7

Figure 5-2

Polymer composite materials formed with MMA are fairly brittle. This is illustrated in Figure 5-3. Curve a, for an MMA-containing PC, indicates that the composite cannot maintain a load once the ultimate stress is reached. The brittleness of this material can be greatly reduced by the addition of a comonomer such as butyl acrylate. MMA and butyl acrylate readily react to form a copolymer that is relatively tough and not subject to complete failure at its ultimate stress. Additions of 5 and 20% butyl acrylate to MMA and their respective composites gave the compressive stress-strain results shown by curves b and c in Figure 5-3. Although there is an accompanying reduction in the ultimate stress, some applications might be better served with a more ductile material.

2. Laboratory Testing of Polymer-Concrete

Compared with the extensive testing program to determine the properties of PIC, the PC evaluation effort at BNL and the USBR has been small. To date, only a few of the mechanical and durability properties have been measured.

One detailed evaluation was performed at the USBR.[5] In the initial work, a graded sand-aggregate mix closely approximating that of CP-type concrete[1] was integrally mixed by hand with catalyzed MMA and polymerized at 70°C. The heat generated during polymerization of these specimens was quite high, and as a result the samples developed relatively low compressive strengths, of the order of 8000 to 12,000 psi. Subsequent work on the method and incremental temperature control during polymerization resulted in more consistent specimens with compressive strengths of 11,000 to 12,000 psi. The addition of cross-linking and coupling agents, glass fiber reinforcement, and a change to a tert.-butylazoiso butyronitrile catalyst improved the strength to 14,800 psi.

Development of the method has continued, and in its present form oven-dried Clear Creek aggregate is machine mixed with the monomer system, placed in molds, and polymerized at room temperature by the promoter-catalyst technique. The specimens are prepared with 7 to 8% monomer by total weight of the wet mix. Depending on the maximum size of the aggregate and the amount of cross-linking agent in the monomer system, the specimens develop average compressive strengths varying from 18,400 to 20,000 psi. These mixes have produced very consistent specimens with individual strengths that vary <2% from the mix average.
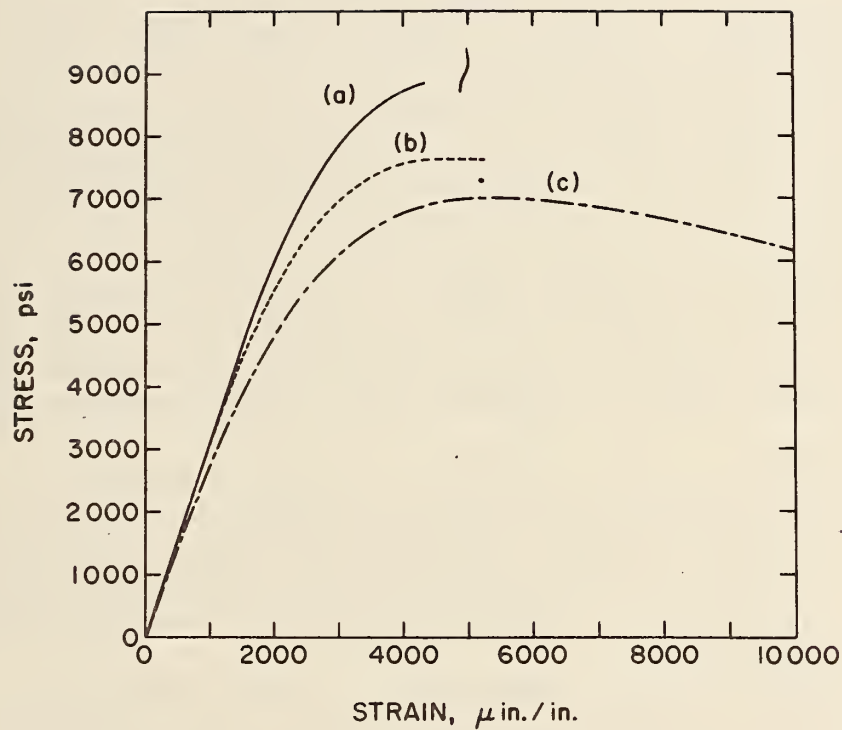
Figure 5-3 Compressive stress-strain curves for polymer-
concrete. Curve *a*, MMA; curve *b*, 95 wt % MMA – 5 wt
% butyl acrylate; curve *c*, 80 wt % MMA – 20 wt % butyl
acrylate.

Specimens prepared with use of conventional concrete mixing procedures and room-temperature polymerization have been tested for compressive stress-strain, tensile splitting, unit weight and specific gravity, and water absorption (see Table 5-3). Other specimens were exposed to a 5% H_2SO_4 solution for two months without any apparent effect on their properties.

Creep tests have also been performed on PC specimens containing MMA. The tests were conducted using 6-in.-diam x 12-in.-long cylinders that were subjected to compressive stresses of 800, 1301 and 3938 psi for 63 days. The stresses were ~5, 8, and 24%, respectively, of the ultimate compressive strength. After 63 days the specimens exhibited less creep than normal-weight concrete. The unit creep deformation (μin./in./psi) of PC specimens under the 3938 psi compressive load was very close to that of unimpregnated CP-type concrete under a compressive load of 2313 psi.

PC development work at BNL has been focused primarily on highway applications such as repairing holes or as an impervious overlay on bridge decks. Criteria considered essential for these applications are the ability to be mixed and placed conventionally, rapid predictable polymerization rates over a wide range of temperature, high strength, and good bonding.

Several studies were performed to select aggregate size distributions that will produce high strength - low porosity materials. To date, the best results have been obtained using a dried dense graded aggregate mix used on Long Island in asphaltic concrete. A sieve analysis of this material was given in Table 5-2.

Experiments were performed with the MMA-TMPTMA and polyester-styrene monomer mixtures. The results indicate that high-strength materials (compressive strengths >10,000 psi) with low water absorptions (<0.5%) can be produced with polymer concentrations of 9.1 wt %. The water absorptions are similar to those of PIC.

Shear tests have been performed to determine the bonding characteristics of PC when applied to steel or sound concrete surfaces. Two monomer systems, 60 wt % styrene - 40 wt % TMPTMA and 53 wt % polyester - 28% styrene - 19 wt % TMPTMA, were used to produce PC, which was applied as 3/4-in.-thick liners on 6 and 8-in.-diam steel pipe. A shear strength of 1100 psi was measured for PC applied to sand-blasted steel surfaces, and 400 psi was obtained for samples that had not been sand blasted.

PROPERTIES OF POLYMER CONCRETE

6-inch by 12-inch cylinders

Test	Temperature	Result
Compressive Strength *	-15°F	24,800 psi
	70°F	19,600 psi
	120°F	15,800 psi **
	190°F	14,100 psi
Tensile Splitting *	-15°F	1,510 psi
	70°F	1,430 psi
	190°F	1,370 psi
Modulus of Elasticity *	-15°F	6.11×10^6 psi
	70°F	5.28×10^6 psi
	190°F	4.44×10^6 psi
Poisson's Ratio *	-15°F	0.24
	70°F	0.23
	190°F	0.22
Unit Weight *	--	149.1 lb/ft^3
Specific Gravity *	--	2.40
Water Absorption ***	--	0.6 percent

Specimens prepared with 8-% monomer by total weight. Monomer system consisted of 97.5-% MMA + 2.5-% TMPTMA.

* Average value for 3 specimens.

** Value for single specimen

*** Average value for 2 specimens

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Cores taken from concrete specimens containing 6-in.-thick PC overlays were subjected to shear strength measurements. Bond strengths at the PC-concrete interface of >1000 psi are normally obtained.

Preliminary tests have been performed to determine the coefficient of thermal expansion for PC. PC specimens containing a 15% concentration of 75 wt % styrene - 25 wt % polyester exhibited an average value of 8.2 μin./in./$^\circ$F. The coefficient is expected to decrease with decreasing polymer concentration. Measurements made at the USBR [4] on unimpregnated normal-weight concrete and PIC containing 5 wt % styrene indicated values of 4 and 5 μin./in./$^\circ$F, respectively.

The largest laboratory tests performed to date at BNL consisted of the pouring of a series of 4 x 4 x 1-ft slabs. This work was performed in support of the field experiments described below. Polymer-concretes containing 13 wt % of a 95 wt % MMA - 5 wt % TMPTMA monomer mix and 10 wt % of 54 wt % polyester - 46 wt % styrene were used. The materials were mixed and placed conventionally. Both systems cured in < 60 min, and practically no shrinkage was observed. Cores taken from the MMA-TMPTMA PC indicated compressive and shear strengths of 9600 and 2175 psi, respectively. A similar compressive strength, 9730 psi, was obtained for the polyester-styrene PC. Water absorption measurements on both materials indicated values < 1%. Freeze-thaw testing is in progress; after 300 cycles, no deterioration is apparent.

3. Field Applications of PC

A large ($\sim$1.4 yd^3) PC placement was made on the Major Deegan Expressway in New York City in December 1973.

A 6-ft^3 skip loader was used to mix 900 lb of PC at one time. Of this amount, 87% (783 lb) was the dense binder aggregate previously described, and 13% (117 lb) was monomer (95 wt % MMA - 5 wt % TMPTMA). Since the temperature at the time of the placement was $\sim$10°C, it was decided to use 2% benzoyl peroxide as the catalyst and 2% DMA as a promoter. Another promoter, DMT, was also available in case a faster cure time was needed to prevent leakage or to overcome low ambient temperatures.

The monomer mixture was made at BNL and batched in 5-gal cans containing 29.25 lb of material. The catalyst was mixed in cans painted red, and the DMA was mixed in cans painted black. The DMT and silane were taken in individually batched quantities to be added at the job site if necessary.

The monomer system was delivered to the job site on the day of the placement. After completion of the form work and application of Crisco as a release agent, the placement was started at 12 p.m. For every batch of aggregate, four cans of monomer were added. Two cans containing the catalyzed monomer were added to two cans containing promoted monomer. DMT was added to the promoted monomer when it was determined that the forms leaked. This helped set the mixture in ~10 to 15 min and stopped the leakage. The monomer was mixed in garbage pails and then poured into the mixer, which already had the aggregate in it. The PC was mixed for ~3 min and then was placed into the form. The PC was tamped into place around the rebars and another batch was prepared. In ~1 hr, the placement was completed and the surface was screeded.

During the screeding procedure, some of the 3/4-in. aggregate was pulled to the surface. The surface was then covered with a black polyethylene sheet and the whole mass was allowed to cure for 1 hr. An estimate of the compressive strength was made by using a Windsor probe, and values ranging between 5400 and 8000 psi were obtained. The measured compressive strength of a cylinder cast from the mix was 12,200 psi, and the water absorption was 0.4%. The patch was opened to traffic within 2 hrs of completion of the placement. The top and underside of the section have been inspected on a periodic basis and no significant changes have been noted. A news release issued by the NYS Department of Transportation, Region 10, is quoted.

"By the use of this extremely fast setting concrete the bridge deck was permanently repaired within a few hours and the traveling public was inconvenienced only to the extent of having traffic on the Major Deegan disrupted for a few hours during the non-rush-hour period of the day instead of for several days."

In other cases, such as on the Greenport bridge, where placements were made in July or August when the ambient temperature was ~30°C, the catalyst was mixed in the monomer system at the job site.

Two drums of the monomer mixture were brought to the job site. Catalyst was added to one drum and the promoter was added to the other drum. Since the ambient temperature was high, the catalyst and promoter concentrations were reduced to 1.5%. For each batch of aggregate, the proper amount of monomer was drained from the two barrels of monomer, mixed, and placed in the cement mixer. After mixing for ~3 min, the PC was placed in forms and tamped. When the final placement

was made, sand of 20-30 mesh size was placed on top and screeded. This gave a much smoother appearance and better riding quality.

The Bridge Maintenance Crew of Region 10 has assisted BNL about 6 times in the placement of PC. They have never prepared the monomer system, but they are efficient in the mixing, placing, and finishing of PC composites. Although apprehensive when they first started working with these materials, they now have a better understanding of PC and can see its value as a maintenance tool. This is a good indication that, with the proper training, bridge and highway maintenance personnel can make polymer-concrete composites and use them as an effective maintenance material.

4. Safety

There are certain dangers involved in the handling and storage of the monomers, catalysts, and promoters discussed above. <u>All</u> precautions published by the manufacturers of these materials should be rigidly observed.

Particular care must be taken to avoid mixing promoters directly with peroxide catalysts because the mixture can react explosively. Add all promoters to the monomer and disperse thoroughly. Then and only then should the peroxide catalyst be added.

A safer and highly recommended procedure for making PC composites is as follows: Divide the monomer system into two equal parts, A and B. Add the promoter to Part A and the catalyst to Part B. Take equal quantities of Part A (monomer with promoter) and Part B (monomer with catalyst). Add Part B to Part A and mix thoroughly. Add the mixed monomer system to the aggregate and mix until the aggregate is completely wetted. Pour into a form, compact, finish, and wait until completely cured.

Monomers, catalysts, and promoters are flammable and must be handled with care. <u>Dry chemical fire extinguishers</u> should be available at the working area. Open flames and smoking should be avoided near monomers, catalysts, or promoters. Well-ventilated areas are required, and personnel should wear safety glasses when working with these materials. The monomers have a disagreeable odor, and it is advisable to wear chemical respirators in the event of discomfort. If chemical materials are spilled, they should be soaked up with noncombustable materials such as vermiculite or perlite and then placed in a shallow trench and ignited with a torch from a safe distance.

If large quantities of monomer are to be disposed of and burning is unacceptable, they can be polymerized in open cans. The resulting polymer can be used as land fill. Figures 5-4 to 5-7 show the disposal of 10 gal of a styrene-TMPTMA monomer system using promoter-catalyst polymerization at $\sim10°C$. In Figure 5-4, the inner can contains the monomer and the outer can contains ice water. Gel formation of the mixture after ~15 min is illustrated in Figure 5-5. After ~50 min the polymerization is rapid and highly exothermic (Figure 5-6). The reaction is complete after about ~60 min, and the bulk polymer can now be disposed of as land fill. The solid polymer is shown in Figure 5-7.

Stirring equipment should be either air-operated or of the explosion-proof Class I - Group D electrical variety. For small laboratory quantities, magnetic stirrers may be used. The concrete mixers used to form PC composites should have explosion-proof electrical motors or be gasoline engine driven.

Catalysts and promoters should be stored in cool places away from direct sunlight and separate from each other. Refrigerators should have any ignition sources mounted externally. Manufacturers give minimum recommended storage temperatures and shelf lives for all these materials.

It is generally recommended that monomers be stored at 20°C or less. At these temperatures, most monomers have a shelf life of ~6 mo. It has been possible to store monomers for periods of 1 yr or more by carefully monitoring the inhibitor concentration of the monomer. All monomers contain inhibitors that the manufacturers have added to prevent spontaneous polymerization. The inhibitors act as free-radical scavengers and thus prevent free-radical polymerization. As an example, the MMA generally used at BNL has an inhibitor (hydroquinone) concentration of 25 ppm. It is stored in 55-gal drums in what is basically a blow-out shed maintained at $\sim15°C$. Periodically (at least once a month), the inhibitor concentration is checked by the peak exotherm method. In this method, a known quantity of catalyst is added to a given volume of monomer (generally 10 cc) and placed in a constant temperature bath, and the peak exotherm is measured as a function of time. The interval or time to reach the peak exotherm is compared with a calibration curve. If the inhibitor concentration falls below a previously established safety limit (15 ppm), additional inhibitor is added to the drum from which the sample was taken.

Figure 5-4. Disposal of catalyzed monomer by polymerization. Initiation of polymerization.

Figure 5-5. Disposal of catalyzed monomer by polymerization. Gel formation after reaction time of ≈ 15 minutes.

Figure 5-6. Disposal of catalyzed monomer by polymerization. Rapid polymerization after reaction time ≈ 50 minutes.

Figure 5-7. Disposal of catalyzed monomer by polymerization. Reaction completed.

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A study was made of the shelf life of MMA monomer catalyzed with benzoyl peroxide, AIBN (Vazo 52) and butylazo-isobutyronitrile (A79). In each case, 1% catalyst was used. About 1/2 liter of the monomer was mixed with the above-mentioned catalysts in glass beakers and covered with aluminum foil. The beakers were placed in an air-conditioned room with a temperature of 23°C. At various times 10 cc of monomer was placed in a constant temperature bath at 70°C and the time to the peak exotherm was measured. The monomer containing AIBN showed an onset of polymerization after 10 days. The A79 and benzoyl peroxide systems remained essentially stable for a period exceeding 23 days although decreases in peak exotherm time of 10 and 21%, respectively, occurred.[5]

5. Summary

Polymer concrete has the potential of combining the premix characteristic of portland cement concrete with strength and durability properties approaching those of polymer-impregnated concrete. Because of its premixed nature, quick cure time at ambient temperature, and high strength, polymer-concrete appears suitable for use in the repair of highway structures, where traffic conditions allow closing of the area for only a few hours.

Field testing of materials containing MMA-TMPTMA and polyester-styrene has been in progress for about three years and to date no detrimental effects have been noted. The most severe test to date has been on a major arterial highway in New York City, where a 3 x 10 x 1.25-ft hole through a bridge deck was filled with a polymer-concrete containing 13 wt % of a 95 wt % MMA - 5 wt % TMPTMA mixture. Polymerization was completed within 1 hr, and traffic was restored 2 hr after completion of the placement. After 12 mo. in service, no deterioration is apparent. It is hoped that the use of PC has resulted in permanent repair of the bridge deck. All the work was confined to the non-rush-hour period of the day and the traveling public was inconvenienced for a few hours rather than for several days. With further experience with PC, the repair time could undoubtedly be reduced.

CHAPTER VI
THE ROLE OF POLYMER IN POLYMER-IMPREGNATED CONCRETE
A. Auskern and W. Horn

Introduction

The incorporation of a relatively small volume of rigid polymer in the pores of concrete results in significant increases in its mechanical and elastic properties. The nominal compressive strength of concrete (4000 to 6000 psi) is increased by factors of 4 to 6. Young's modulus is approximately doubled. Along with these dramatic improvements in mechanical properties, the durability properties of the polymer-impregnated concrete are greatly enhanced. This improvement probably results from the sealing of the concrete by the polymer from the corrosive agent.[1]

The improvement brought about by combining a relatively low modulus polymer ($E \approx 0.4 \times 10^6$ psi) with a higher modulus material ($E \approx 2$ to 3×10^6 psi) to give a product, PIC, with an even higher modulus (≈ 4 to 6×10^6 psi) is upon initial consideration surprising. This result suggests that a unique interaction occurs between the polymer and the concrete.

In an earlier work Auskern[31] and Auskern and Horn[32] suggested that the role of polymer is twofold: to increase the strength of the hardened cement paste and to improve the bonding between the matrix and aggregate. Manning and Hope[33] reached similar conclusions. Gebauer, Hasselman, and Thomas[34] in work on polymer-impregnated porous ceramics, conclude that strength improvements can be attributed to "mechanical reinforcing."

In this chapter the interaction between polymer and concrete is investigated in terms of composite theory. The approach taken differs somewhat from that of Manning and Hope,[33] and is similar to that used by Hansen.[35]

The predictions of composite theory are compared with experimental results, and the results are extended to include a discussion of control of the fracture mode of polymer-impregnated concrete.

1. Polymer-Impregnated Cement and Concrete

Normal concrete consists of particles of fine and coarse aggregate dispersed in a matrix of hardened cement paste. The aggregate volume in normal concretes is around 65 to 70%. The remaining volume is the hardened cement paste matrix. Since sand and stone aggregates have very little porosity, the bulk of the porosity of concrete is in the cement (matrix) phase. The polymer in PIC must therefore be concentrated in the cement phase.

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Porosity in cement has been studied for many years.[36-38] For hydraulic setting materials, like portland cement and plaster of paris, a large volume of porosity is inherent in the set structure. This porosity derives mainly from the excess water required to lubricate the powders so that the material may be placed and is called capillary porosity. The amount of capillary porosity present at any time depends on the original water-cement ratio (W/C) and the maturity, or degree of hydration, of the cement paste. For a mature paste with W/C=0.5, the volume of capillary porosity is about 0.25 cm^3/g of dry paste. If the density of the cement paste is 1.4 g/cc, the equivalent pore content is 35%. If the cement is in a typical concrete, the porosity of the concrete is 10 to 12%. If all these pores are filled upon monomer loading, a weight loading of 7 to 8% is calculated. Because of compositional variations, most normal concretes indicate polymer weight loadings of between 5 and 8%.[1]

Polymer-filled or partially filled voids or bubbles are frequently observed on cut and polished surfaces of PIC[1] (see Figure 6-1). These may vary from large, irregularly shaped air voids that result from entrapped air in the mix, to the much smaller (~0.003-in.-diam) spherical bubbles intentionally introduced via air entraining agents. The entrapped air volume may be ~1% of the concrete volume, and the entrained air volume, as much as 5%[39]. Thus for a concrete with 12% porosity computed from the cement phase, there would be an additional 5% volume from entrained air and ~1% volume from entrapped air. The total pore volume is now 18%. However, the bulk of the porosity (>65%) still lies within the cement phase. Since the average capillary diameter for mature pastes is 0.5 microns,[38,40] most of the polymer present is invisible to the naked eye. Even when viewed at a magnification of 1000, the 0.5-μ pores would be at the practical limit of detectability.

The polymer structure should approximate a negative replica of the cement pore structure. Since the pore structure is a three-dimensional network of connected irregular channels,[38] the polymer should resemble a three-dimensional fibrous network. Some time ago [2] polymer was extracted from a polymer-impregnated cement by preferential dissolution of the cement phase. A three-dimensional fibrous network was observed (see Figure 6-2). The fibers are estimated to be ~0.2μ in diameter, which is the order of magnitude of the pore diameters.

Auskern and Horn[32] showed a fractured surface of polymer-impregnated cement at lower magnification (x200) before and after polymer extraction. These pictures are reproduced as Figures 6-3 and 6-4. The fractured surface (Figure 6-3) was relatively smooth and featureless and had no distinguishable polymer phase. After polymer extraction by dissolution in acetone, the polymer-free
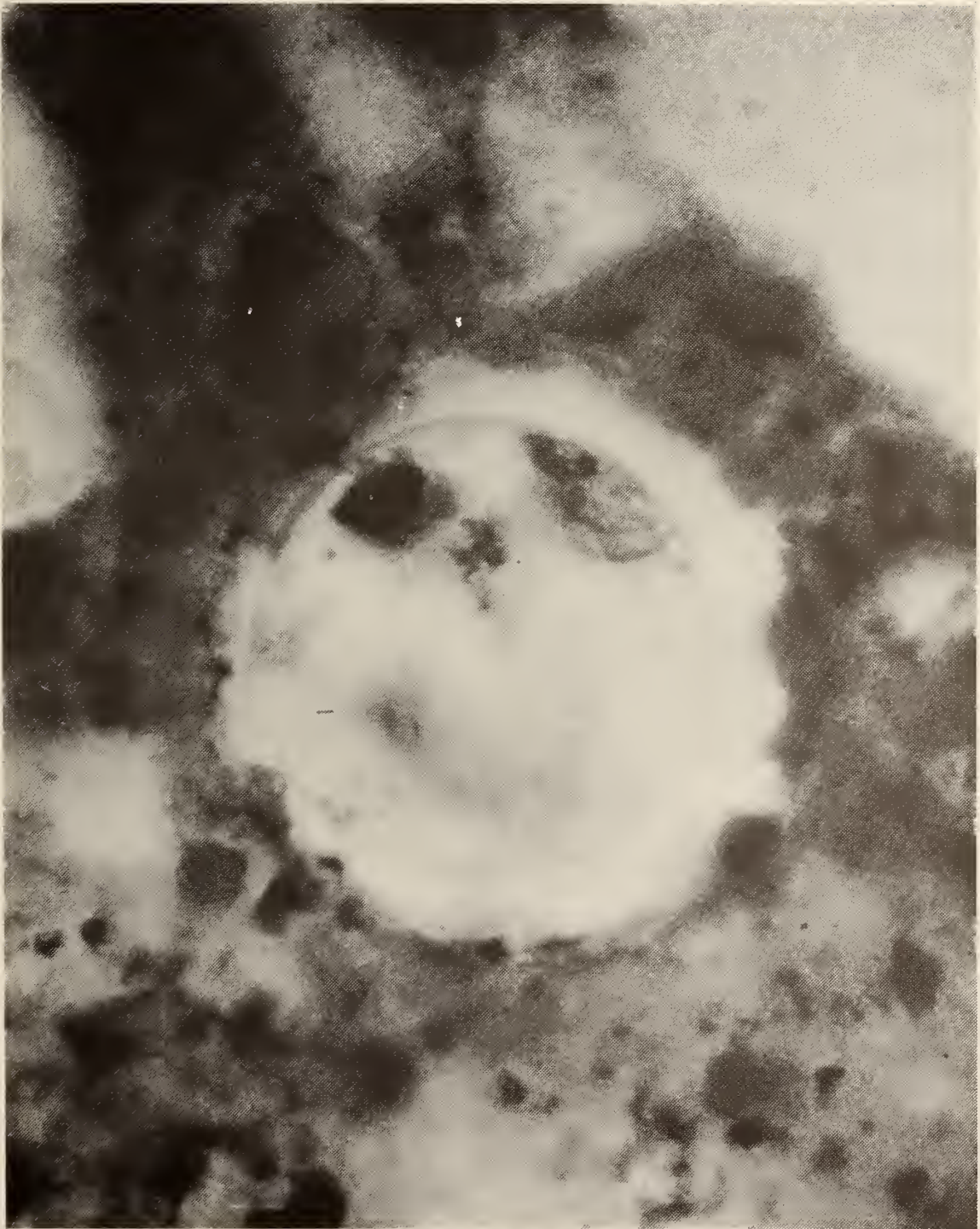
Figure 6-1. A void in polymer-impregnated concrete lined with polymer
x 250. (From Ref. 2.)

Figure 6-2. Polymer extracted from a cement-polymer specimen.
(From Ref. 2.)

Figure 6-3. Fractured surface of cement-polymer viewed with scanning electron microscope x 200. (From Ref. 33.)

Figure 6-4. Sample in Figure 3 after 1 hour in acetone x 200.
(From Ref. 33.)

surface showed considerable roughness (Figure 6-4). This indicated that there was polymer in the as-fractured surface that could not be directly detected as a unique phase. The smallest features readily revealed by "etching" the surface have diameters of <1 to 2 μ.

At still lower magnifications (~x1) the presence of polymer is revealed by a darkening of the cement, as indicated in Figure 6-5 for a fractured polymer-impregnated cement. It is not readily apparent why this should be, since the polymer is colorless. It may be a manifestation of the way in which light is reflected from polymer-filled pores.

2. PIC as a Composite Material

Concrete can be considered to be a composite material because it is a combination of a dispersed phase (the fine and coarse aggregates) held together by a matrix phase. Since the properties of the fine aggregate (sand) are usually different from those of the coarse aggregate, it is sometimes convenient to consider the composite as a coarse aggregate dispersed in a mortar matrix.

The mortar is also a composite system, consisting of a fine dispersed phase in the hardened cement matrix. From a knowledge of the properties and concentrations of the matrix phase, fine aggregate, and coarse aggregate, and with use of the appropriate composite model, the properties of concrete can be derived by first combining the cement and sand to form the mortar and then adding the coarse aggregate to the mortar matrix. Hansen[35] has used this approach.

The material becomes more complex when polymer is added to the system. The polymer fills the pores of the hardened cement paste phase, which creates still another composite material, the hardened cement paste - polymer system. Polymer-impregnated concrete can then be considered a composite of coarse and fine aggregate in a matrix of polymer-impregnated cement. The problem in composite theory is then to predict first the properties of cement when it is polymer-impregnated, then the properties of the composite formed when fine and coarse aggregates are added to the polymer-impregnated cement matrix.

Significant progress has been made in composite theory and composite materials development in the past few years, mainly because of the quest for high-performance lightweight materials for aerospace applications. Most of these advances have been in the area of fiber-reinforced materials. Theoretical aspects for this type of composite are well developed.[41] The theory is less well developed for particulate systems, such as concrete. However, several workers have developed composite models based on the structure of concrete.[42] One such recent concrete model is due to Hobbs,[43] and is a special case of a more general solution
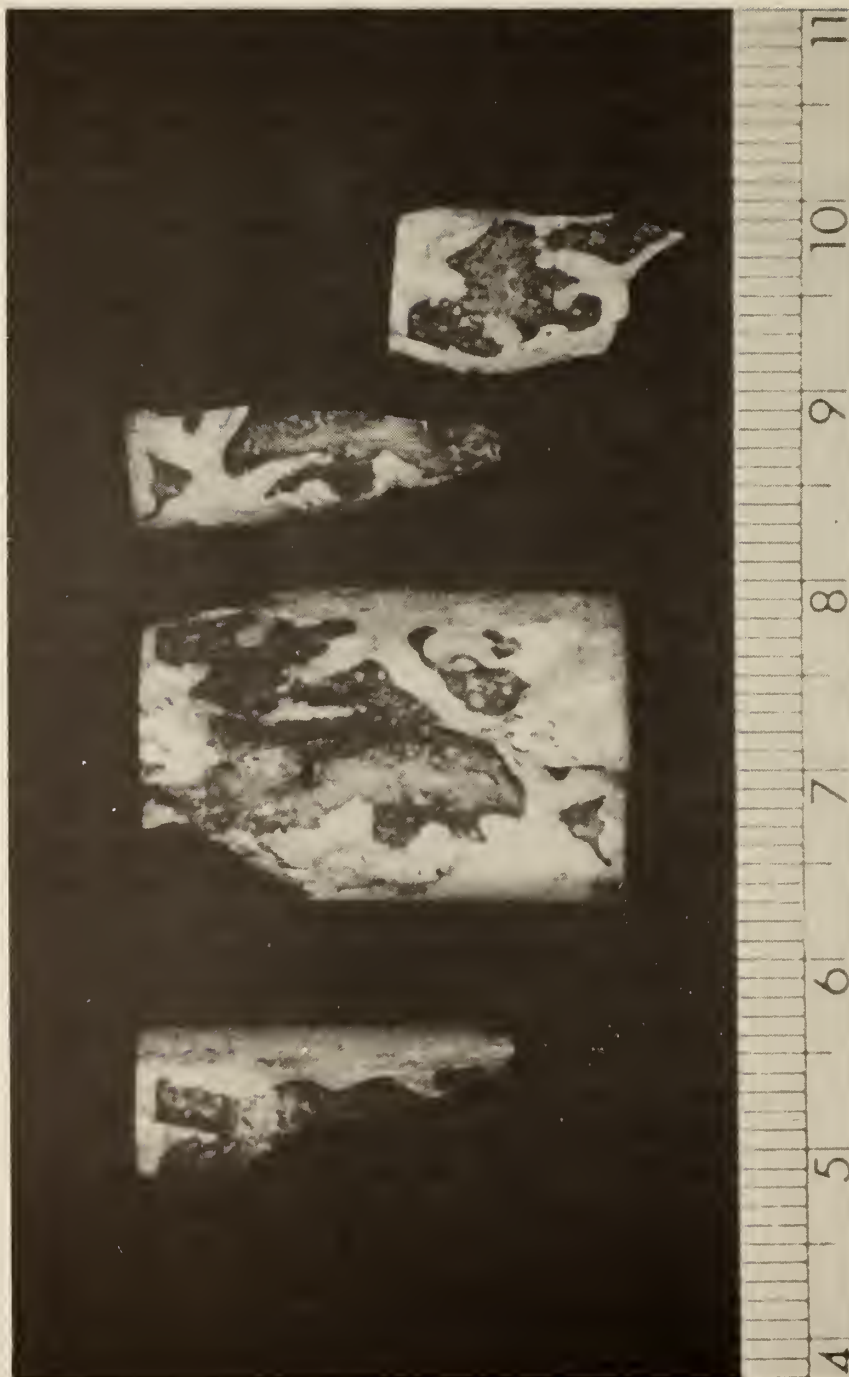
Figure 6-5. Fractured polymer-impregnated cement specimen. The dark
region is polymer filled x 2. (From Ref. 2.)

derived by Haskin and Shtrikman.[44] Hobbs's model will be used
here, since it does not give results significantly different from
those of other workers and is convenient to handle. Manning and
Hope[33] used Counto's model.

Hobbs's model can be put into the form

$$\frac{E}{E_m} = 1 + \frac{2V_a \ (r - 1)}{(r + 1) - V_a \ (r - 1)} \tag{1}$$

where E = Young's modulus of the composite,

E_m = modulus of the matrix,

V_a = volume fraction of aggregate,

$r = E_a/E_m$, where E_a is the modulus of the aggregate phase.

Equation (1) was derived for particulate composites. As
shown earlier, impregnated composites are not particulate; the
polymer assumes the structure of the continuous intersecting
three dimensional pore network. Krock[45] compared dispersed
particle and continuous-skeleton metallic composites of the same
composition and concentration range. He observed no significant
difference in the modulus of elasticity of the two different com-
posite structures. Equation 1 will therefore be used to predict
the modulus of polymer-impregnated cement. To apply Eq. (1), E_m,
the modulus of pore-free cement must be known. There are a number
of ways in which this can be estimated. In certain cases Eq. (1)
can be used with r = 0 and $V_a = V_p$, the volume of porosity. This
model gives results similar to the MacKenzie model[46] for the
effect of porosity on modulus, where the modulus varies approxi-
mately as $(1 - V_p)^2$. However, Helmuth and Turk[47] have shown
that the modulus of cement varies as $(1 - V_p)^3$.

A hardened cement paste containing about 40% porosity was
prepared. The Young's modulus was 1×10^6 psi. Applying the
relationship of Helmuth and Turk[47] results in $E_m = 4.6 \times 10^6$ psi
for a hypothetical pore-free cement. By using this value for E_m
in Eq. (1), the modulus of the polymer-filled cement can be
computed. For this example the computed composite modulus is 2.3
$\times 10^6$ psi. Experimentally a modulus of ~2.8×10^6 psi for the com-
posite, compared with the unfilled modulus of 1×10^6 psi, is ob-
served. Thus, from both theoretical and experimental considera-
tions, it is seen that incorporation of the rigid polymer into the
porous cement phase results in a cement phase of greatly increased
stiffness.

Equation (1) can also be applied to mortars. The aggregate
phase now consists of sand particles of modulus ~10×10^6 psi, and
the matrix is either normal cement of modulus 1×10^6 psi or

polymer filled cement of modulus 2.8×10^6 psi. The moduli of the two mortars can be calculated for various aggregate loadings. This is illustrated in Figure 6-6, where the theoretical curves predicted from Eq. (1) are presented along with Young's modulus for a series of normal and polymer-filled mortars with sand contents ranging from 40 to 65 vol %. The calculated results are in fairly good agreement with the experimental results, although the agreement appears better for the polymer-filled series. These results indicate that for mortar the only effect of the polymer is to increase the modulus of the cement phase.

Some concretes were next investigated by adding -3/8+4 mesh limestone aggregate to mortar in concentrations of 10 to 50 vol %. The expected moduli of the concretes were calculated from Eq. (1) by using 8×10^6 psi as the modulus for the limestone aggregate (estimated from sonic velocity measurements) and the observed modulus of the 40% sand mortar. These results are shown in Figure 6-7. Here the experimental results lie below the calculated curves and indicate an extrapolated mortar modulus (0% aggregate) lower than that used for the calculation. The reason for this discrepancy is not clear. The results do, however, have some interesting features that are pertinent to composite theory. For the unfilled concrete there is very little compositional dependence of the modulus. The polymer-filled concrete indicates a compositional dependence of approximately the proper magnitude. This suggests that composite action is occurring for the polymer-filled concretes and is not occurring for the unfilled concretes. That is, for the unfilled concrete, advantage is not being taken of the relatively high aggregate modulus. This usually happens when there is poor bonding between matrix and aggregate phases. Thus the presence of polymer appears to improve the bonding between the matrix and aggregate.

In another test concrete, the limestone aggregate used previously was replaced by steel (modulus, 30×10^6 psi). Equation (1) predicts a composite modulus, for 40 vol % steel aggregate, of about 8×10^6 psi for the unfilled concrete. Measurements indicated a modulus of 7.0 to 8.2×10^6 psi for the polymer-filled concrete, in very good agreement with the predictions. For the unfilled concrete the agreement was very poor. An experimental modulus of $\sim 1 \times 10^6$ psi was indicated. These results again suggest that in the unfilled concrete advantage is not being taken of the high aggregate modulus.

The measurements so far show that polymer-impregnated concretes behave more like composite materials than do normal (unimpregnated) concretes. Normal mortars, however, do indicate composite action, which must arise through better bonding between the matrix and small sand particles. Thus it seems that the presence of the polymer serves two functions. The modulus of the matrix phase is increased, and bonding between the matrix and coarse aggregate is
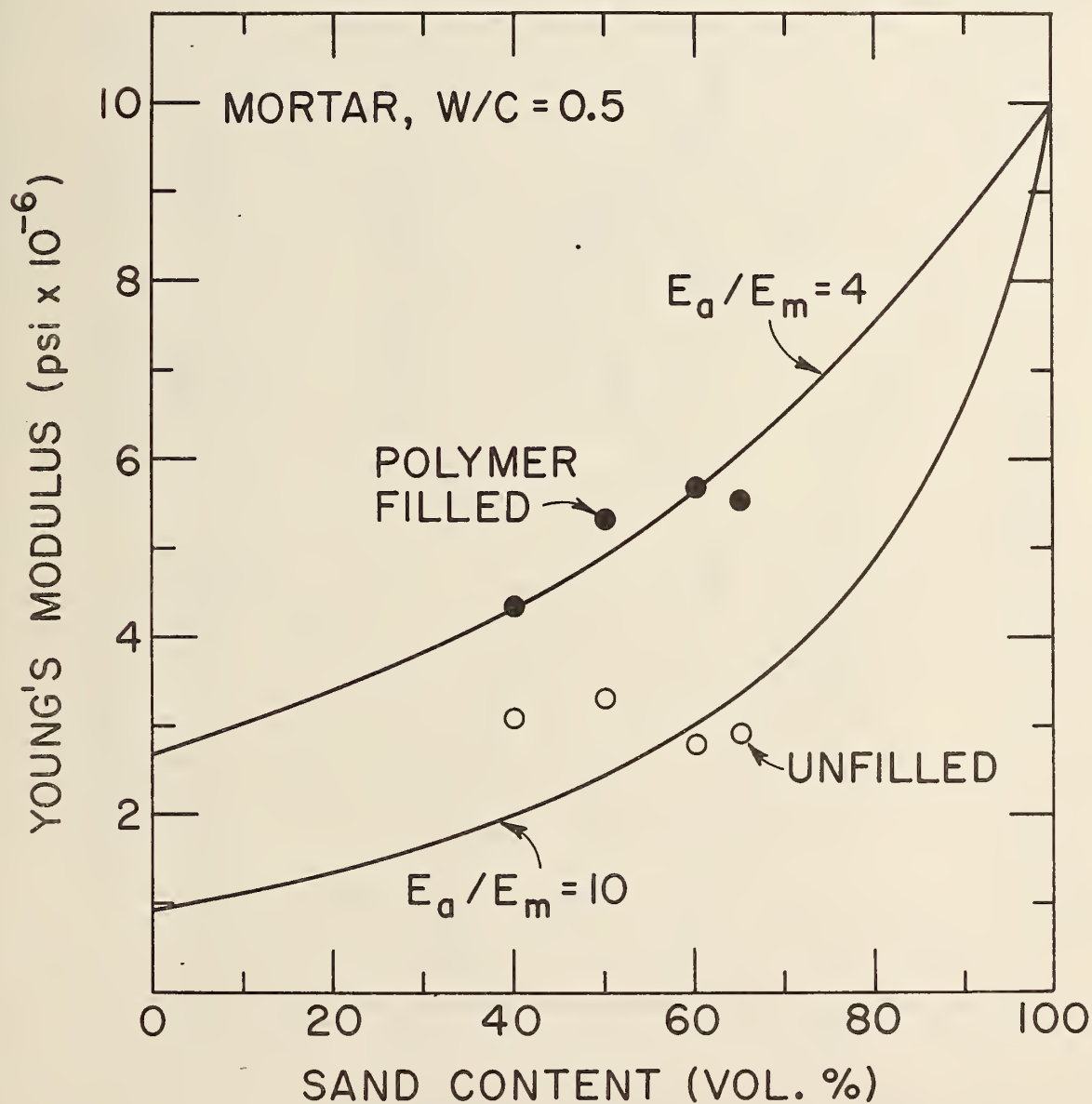
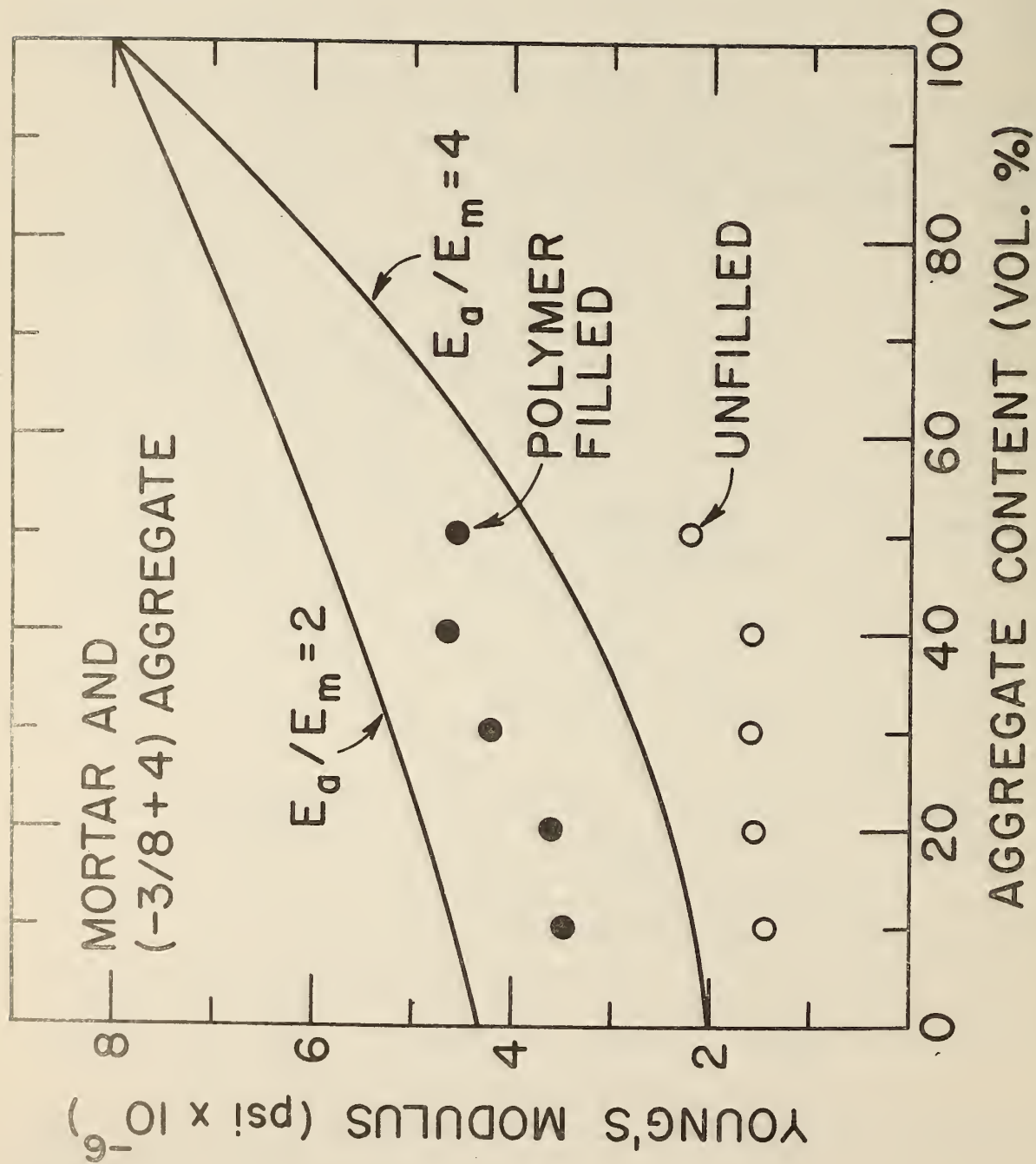Figure 6-6. Predicted and experimental variation of Young's modulus of mortar with sand content.

Figure 6-7. Predicted and experimental variation of Young's modulus of concrete with −3/8+4 mesh aggregate content.

improved. So far, composite theory has been applied to predicting Young's modulus of normal concrete and PIC. The fracture mode and the strength of PIC are next discussed.

3. Fracture Mode of PIC

The fracture of normal concrete has been studied in detail by many investigators. Shah and Winter[48] have demonstrated that in compression the mortar-aggregate interface is first to fail. The progressive failure of this interface and the enlargement and joining of cracks lead to the significant inelasticity of concrete and the typical curvilinear stress-strain curve.

It was reported earlier [32] that the fracture modes of concrete and PIC are different. This is illustrated in Figure 6-8, where PIC and normal concrete are shown after failure. PIC shatters on failure. The fracture surfaces pass through the aggregate particles, and thus the matrix-aggregate bond strength is greater than the strength of the aggregate. Stress-strain curves for normal concrete and PIC are shown in Figure 6-9. PIC shows nearly linear behavior to failure, which is typical of brittle material.

The brittle nature of PIC presents a design limitation. It would be desirable to modify this behavior to produce a material with the slow failure mode of normal concrete while retaining the high strength and modulus of PIC.

One approach to this problem is to adjust the matrix-aggregate bond so that the failure mode, as in normal concrete, becomes failure of this bond. In principle this can be done by using a very strong, tough aggregate. If the aggregate is strong enough, an impinging crack will be diverted around the aggregate rather than through it.[49] This is essentially the condition with the PIC prepared with steel aggregate (see previous section). The stress-strain curve for this material is shown in Figure 6-10. The failure mode is no longer brittle, but much like that of normal concrete. At 1% strain the material still supports >60% of the ultimate load. Fractured steel aggregate concretes are illustrated in Figure 6-11.

The fracture mode of PIC can also be altered from a brittle one to one like that of normal concrete by incorporating a small quantity ($\sim$1 vol %) of fiber in the matrix. The fiber does not affect the modulus of the concrete because the concentration is so low. Some experiments were performed on a mortar containing 1% steel fibers (1/4 in. long by 0.010 in. in diameter). The stress-strain curve for this material is also shown in Figure 6-10. At 1% strain the material still supports $\sim$80% of the ultimate load. The fibers obviously serve to inhibit crack propagation through the mortar by providing an energy-absorbing mechanism that is well bonded to the matrix.[50]

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Figure 6-8. Polymer-impregnated concrete (left) and normal concrete after failure (3-in.-diam. x 6-in. cylinders).
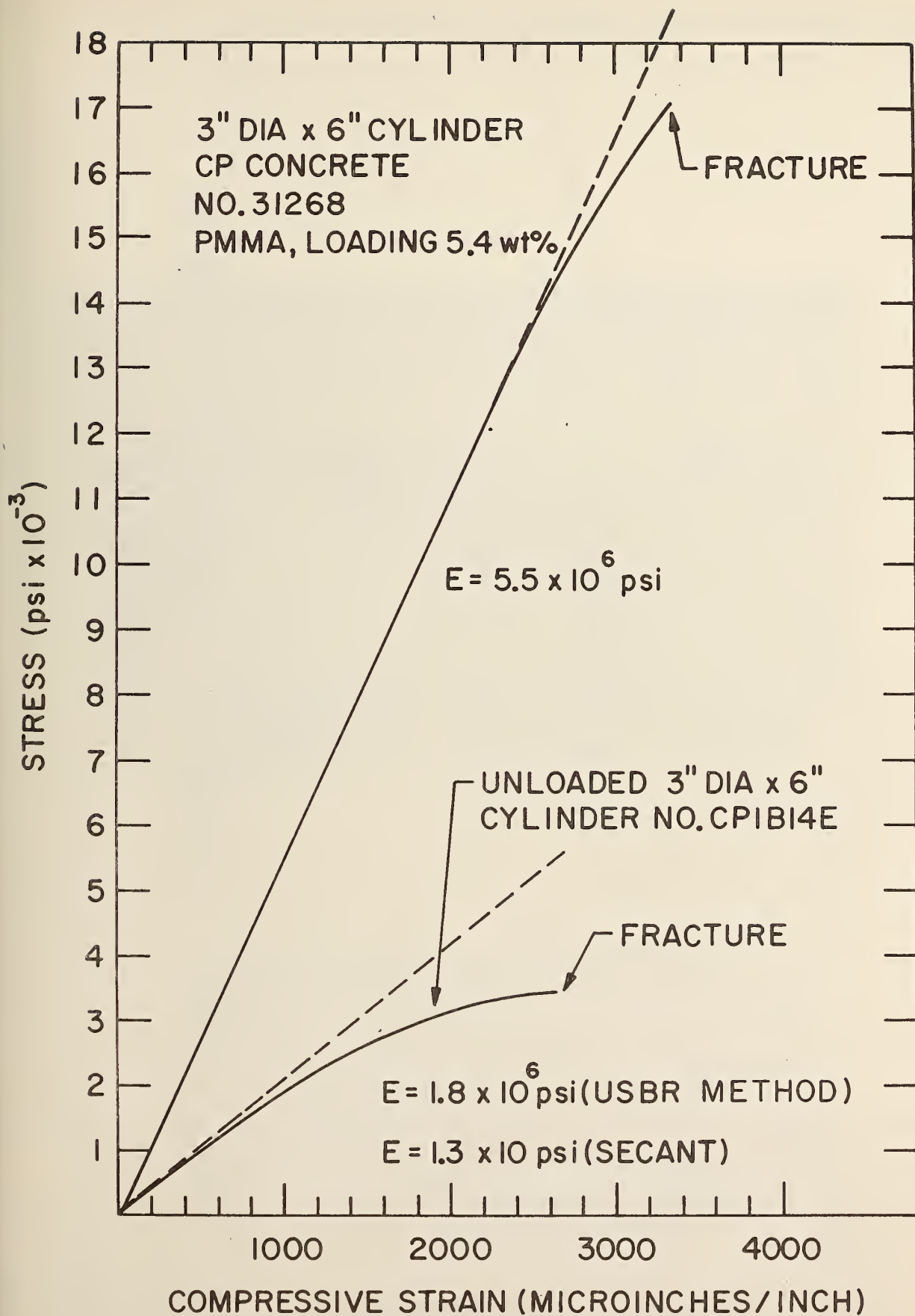
Figure 6-9.   Stress-strain curves for a normal concrete and polymer-impregnated concrete (3-in. diam. x 6-in. cylinders).
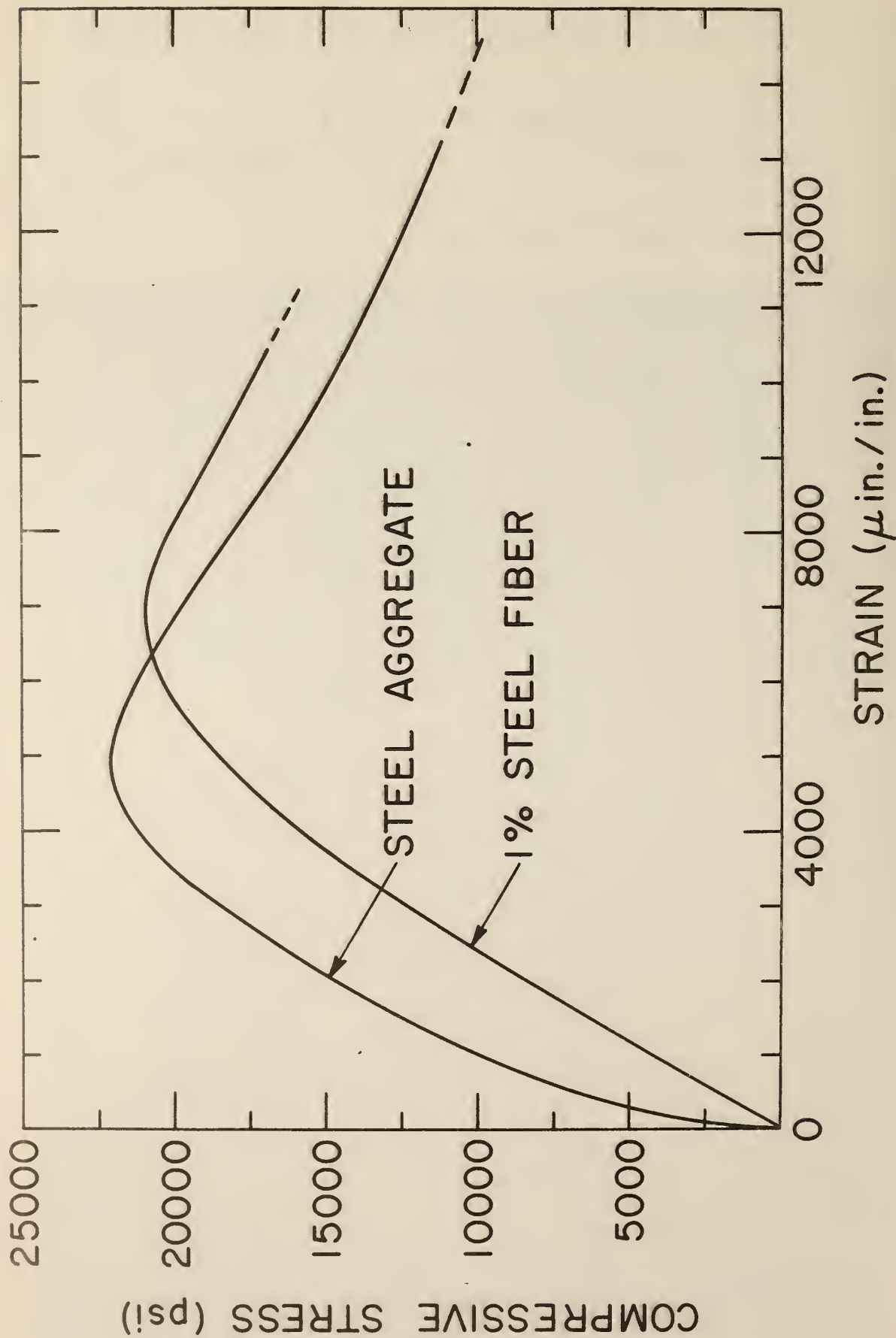
Figure 6-10. Stress-strain curves for polymer-impregnated steel aggregate concrete and polymer-impregnated steel-wire reinforced mortar (1 1/2-in.-diam. x 3-in. cylinders).
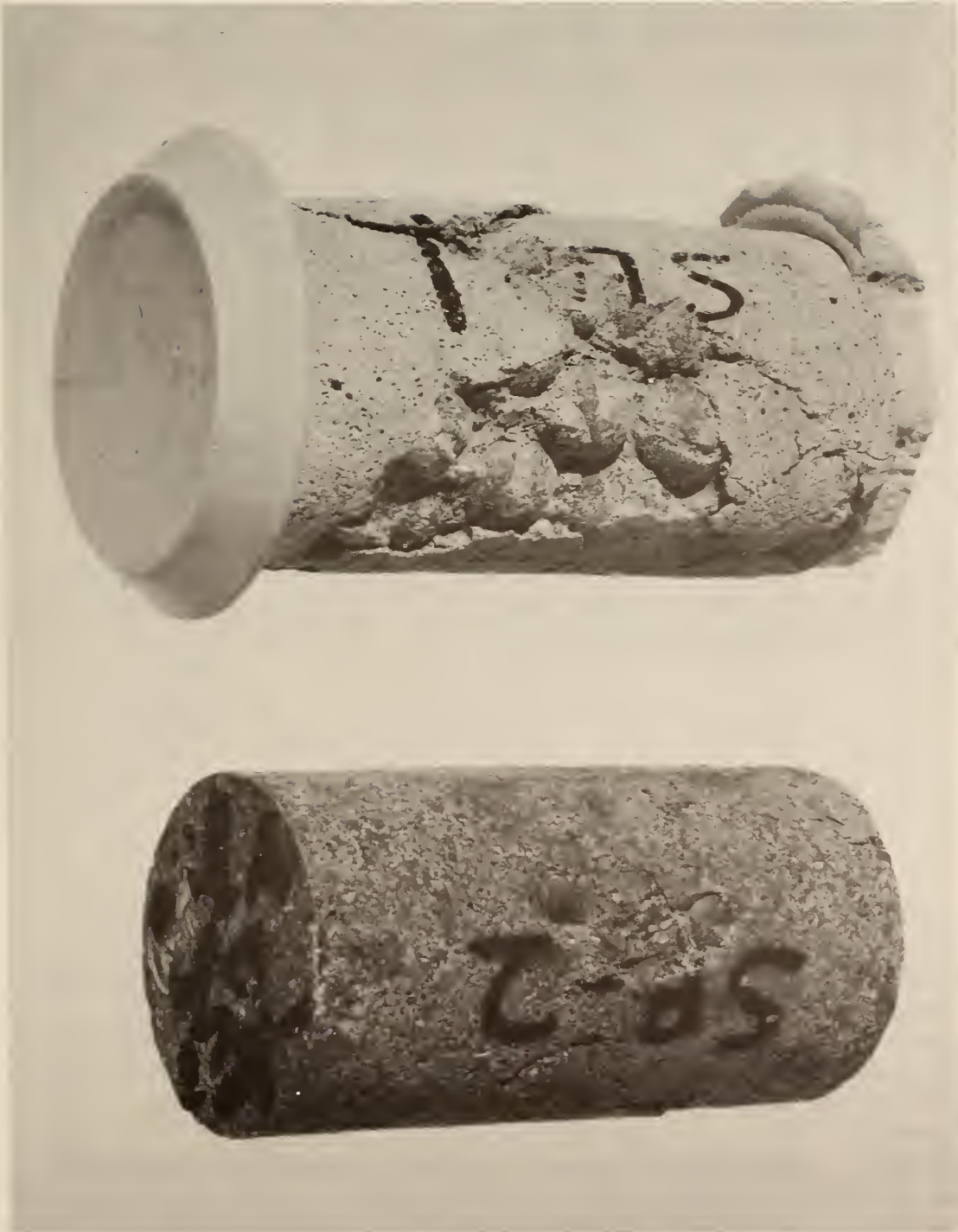
Figure 6-11. Polymer-impregnated steel aggregate concrete (left) and impregnated steel aggregate concrete after failure (1 1/2-in.-diam. x 3-in. cylinders).

Control can be exercised over the PIC fracture mode either by controlling the relative interface-aggregate strength or by providing an energy-absorbing mechanism along the fracture path. Thus the brittle fracture of PIC can be readily changed to one of considerable ductility without sacrificing the desirable strength properties of the material.

4. Strength Improvement of Polymer-Impregnated Concrete

The strength of brittle materials can be predicted by using the theory that Griffiths developed in 1920[51] for the strength of glass. This theory states that

$$\sigma = A \left(\frac{E \gamma}{C} \right)^{1/2} \tag{2}$$

where σ is the fracture strength, A is a geometric factor, and E is Young's modulus; γ is the fracture energy, or the work required to create a unit area of new fracture surface; C is the intrinsic flaw or crack length, or the flaw that under stress eventually grows into the failure crack.

Inspection of the Eq. (2) tells us that the stress to propagate an existing flaw increases with increasing modulus. This has been widely established for concrete. It also seems reasonable that the strength increases with the work of fracture for a brittle material. The smaller the flaw size, the more difficult it will be for the flaw to propagate, and the stronger the material will be.

The Griffiths approach has been used to explain the strength increase of hardened cement paste when it is polymer impregnated.[52] The strength increase, according to Eq. (2), is given by

$$\frac{\sigma_i}{\sigma_u} = \left(\frac{E_i}{E_u} \right)^{1/2} \left(\frac{\gamma_i}{\gamma_u} \right)^{1/2} \left(\frac{C_u}{C_i} \right)^{1/2} , \tag{3}$$

where the subscripts i and u refer to impregnated and unimpregnated, respectively. For hardened cement paste, E_i can be calculated or measured, E_u is generally measured, γ_i can be estimated from the fracture energy of the polymer[51] or measured, and γ_u can be measured. Then, assuming that the flaw length remains unchanged on polymer filling, σ_i/σ_u, which is the factor by which the strength of hardened cement improves on polymer filling, can be computed.

The strength improvement factor was calculated for hardened cements over a range of porosities, and is shown in Figure 6-12, in which data on partially filled cements [32] and estimated strength improvements for partial loadings are also given. It is
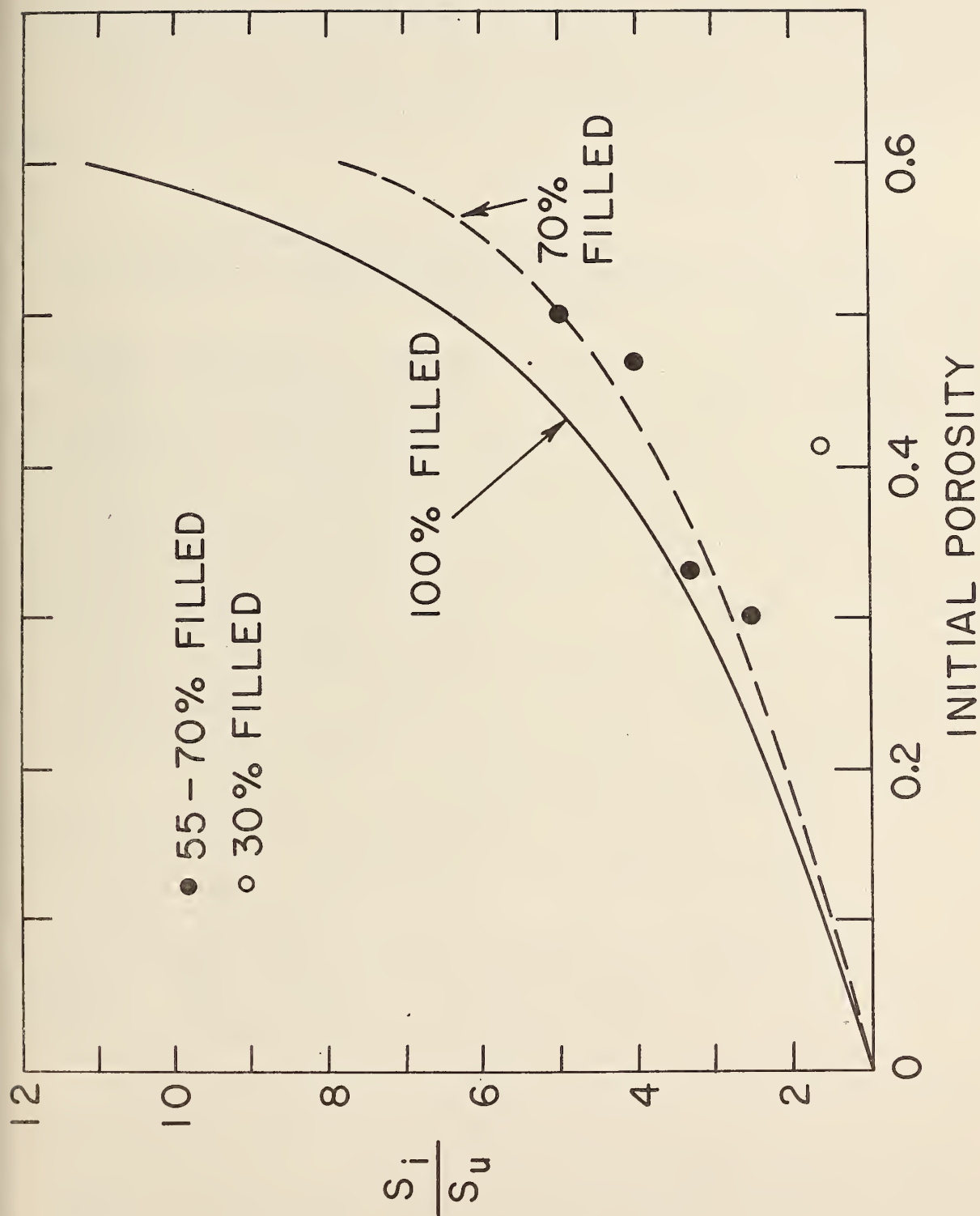
Figure 6-12. Strength increase of fully impregnated hardened cement pastes as a function of initial porosity.

obvious that the higher the porosity the greater is the strength improvement. This arises from the greater amount of polymer in the system and its very high fracture energy. For hardened cements of ~30 to 50% porosity, a range generally encountered in normal manufacturing, the strength upon complete polymer filling increases by a factor of about 3 to 6. If the strength of the unimpregnated hardened cement as a function of porosity is known, the strength of polymer filled vs unfilled hardened cement paste can be plotted. This is done in Figure 6-13 with use of the relationship [31,32]

$$\sigma_p \sim 1.2 \times 10^5 (1 - P)^6,$$

where P is the porosity. It is obvious from Figures 6-12 and 6-13 that, although the strength improvement factor is greater as the porosity increases, the polymer-filled strength is lower, with increasing porosity.

It remains to extend this work to predict the strength improvement of concrete when PIC is formed. For this calculation the fracture energies of unimpregnated and impregnated concrete are required, and these are not known. These values could be estimated if the fracture energy of the aggregate were known. Some measurements of the fracture energy have been reported for quartz and feldspar minerals.[52] These values are around 3×10^4 erg/cm^2, which is about half that for the fracture energy of polymer-impregnated hardened cement paste. For PIC, γ_{PIC} is estimated from a simple mixing rule,[53] assuming a two-phase system. Since failure in normal concrete does not usually involve aggregate, γ_C (the fracture energy of normal concrete) is assumed to be the same as that of hardened cement. Experimentally,[1] and from composite theory considerations,[54] the modulus of concrete increases by a factor of 2 to 3 upon polymer impregnation. Putting these factors in Eq. (3) results in a strength improvement of 3 to 4 times. In view of the simple assumptions made and the lack of good experimental values, the calculated strength improvements seem reasonable.

The improvement in strength of concrete upon polymer impregnation is a direct result of the increase in the elastic modulus and the fracture energy of the materials when polymer-impregnated concrete is formed. These improvements are a direct result of the increase in the elastic modulus and fracture energy of the hardened cement paste phase, and of the improved bonding between the matrix and aggregate phases.

It is also obvious that the stronger the initial cement or concrete, the smaller will be the improvement after polymer filling. This is due to the dual role of porosity. The more porosity present the weaker is the material, but the more polymer it can contain, the relatively greater the strength improvement. There
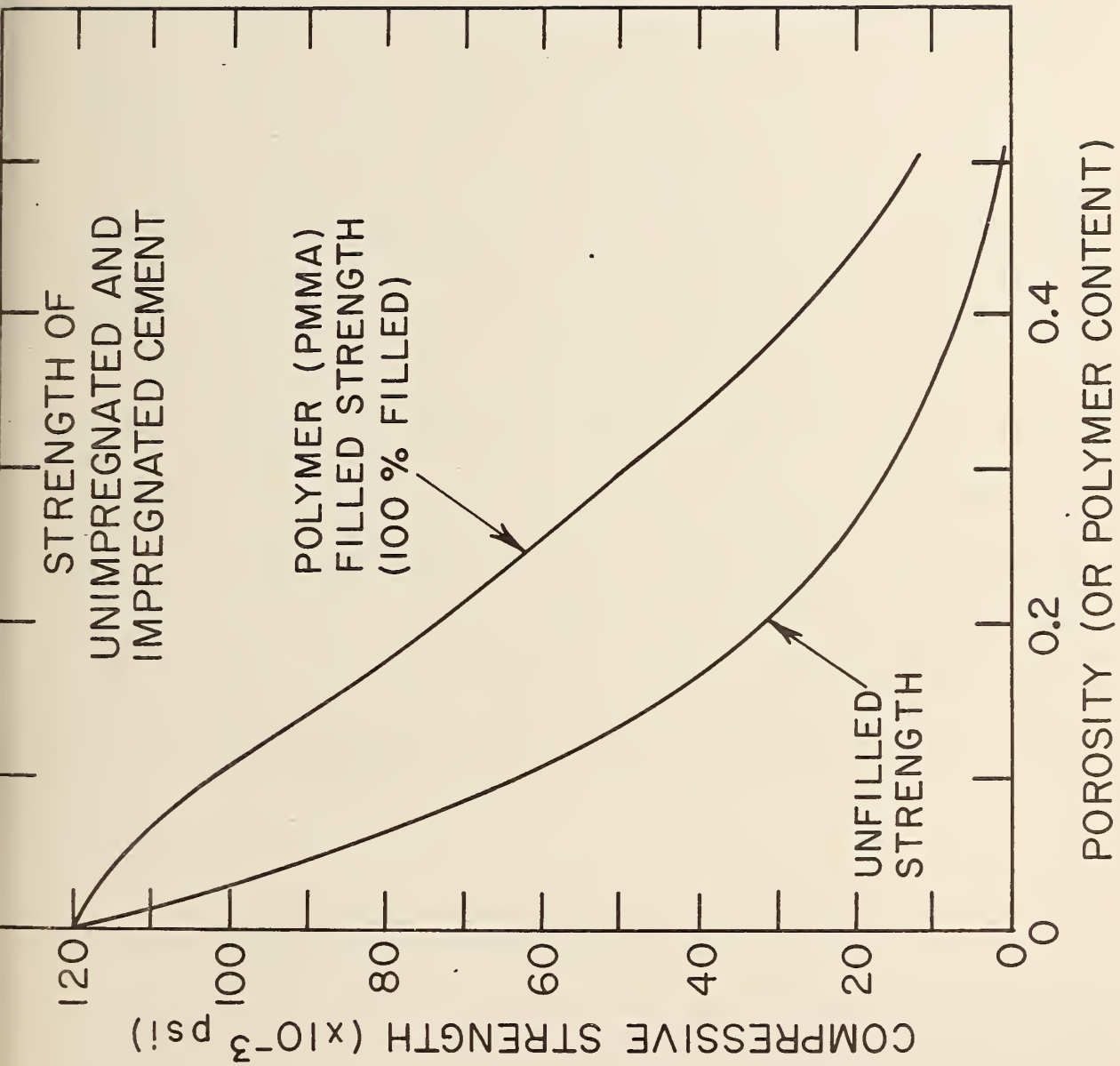
Figure 6-13. Strength of impregnated and normal hardened cement pastes as a function of polymer content or porosity.

is a very important trade-off here between initial strength, final strength, polymer content, and cost, that has not been fully exploited.

QUALITY CONTROL AND NONDESTRUCTIVE TESTING
OF POLYMER-IMPREGNATED CONCRETE
Allan Auskern

Introduction

In normal concrete construction a large variety of testing techniques are used for the purpose of ascertaining whether or not the concrete meets specifications. With the development of polymer-impregnated concrete (PIC) and the interest in it, especially for precast applications, it is important to know whether this material also meets specifications.

The starting material in the preparation of PIC is a cured and dried concrete. PIC results when the pores of this material are filled with a monomer, which is subsequently polymerized. This process results in significant increases in strength properties (generally by factors of 3 to 5) and the elastic properties (Young's modulus generally increases by a factor of ≈2).

A number of the testing techniques used for quality control and nondestructive testing of normal concrete have been applied to PIC. Usually measurements were made on normal concrete and then on PIC prepared from the same specimen. Testing was limited to specimens of a size that could be conveniently handled in a laboratory, although some testing of more massive structures was done. The magnitude and types of changes observed are noted and attempts are made to correlate these with polymer loadings and physical properties. Nine methods considered are as follows: weight change, gamma radiography, neutron radiography, modulus measurements, resonant frequency measurements, impact hammer, sonic velocity, coring, and Windsor probe measurements. This work has been reported in the annual reports on the Concrete-Polymer Program [1-5].

Testing Methods

The various quality control and non-destructive testing methods are discussed below.

1. Weight change.
Initially polymer loadings were determined by weighing the samples before monomer loading and after polymerization. The procedure is convenient for samples of reasonable size. In general, weight increases of about 5 to 7% are found. The method evaluates the whole sample, but it does not detect variations in polymer loading within the sample. It also weighs any unpolymerized monomer and is unsuitable for field operation or for heavy pieces.

2.   Gamma radiography.

Gamma radiation, which is attenuated by concrete, has been used to determine the thickness and density of concrete to accuracies approaching 2% for thick slabs. However, the attenuation by polymer is small. The decrease in radiation intensity of an incident gamma beam passing through PIC is only about 1% greater than that for normal concrete. In addition, the technique cannot distinguish between monomer and polymer.

3.   Neutron radiography.

Neutron radiography should be a promising technique because of the high hydrogen content of organic polymers. Computations for PMMA-impregnated concrete indicate that neutron attenuation is 50 to 70% greater than for unimpregnated concrete. Consequently some unimpregnated, partially impregnated, and fully impregnated concrete samples were examined by neutron radiography.

Two neutron radiographs are shown in Figure 7-1. Polymer-impregnated samples should appear lighter than unimpregnated samples. This was observed in the radiographs, but because of the overlapping and extensive neutron shadows of the stone aggregate, meaningful radiographic density measurements could not be obtained. This technique also cannot distinguish monomer from polymer, or water from MMA. However, the method appears to have potential usefulness for observing gross variations in polymer content within a single sample. The technique would probably be more successful with mortars or small aggregage concrete.

4.   Modulus of Elasticity or Stiffness.

When PIC is formed the modulus increases significantly; therefore, techniques that subject the test specimen to a mechanical load should indicate a reduced deflection. Attempts were made to correlate Young's modulus and the compressive strength of PIC cylinders. When plotted, the data from many series of different concretes, polymers, and drying and curing treatments show considerable scatter. Within individual groups the results are much more consistent. It is widely recognized that the modulus is related to the strength of concrete. This relationship appears to be continuous between normal concrete and PIC (see Figure 7-2).

Modulus or deflection measurements have two important advantages: they reflect the average condition of the whole sample, and they are not confounded by the presence of unpolymerized monomers or water.

This method is also readily adaptable to continuous bridge and highway testing. A number of commercial systems have been developed in which loading devices attached to trucks moving along the pavement automatically measure deflection. Although PIC structures have not been tested in this manner (nor have PC-repaired bridge decks), this technique appears appropriate for evaluating the changes brought about by polymer-impregnating the pavement surface.
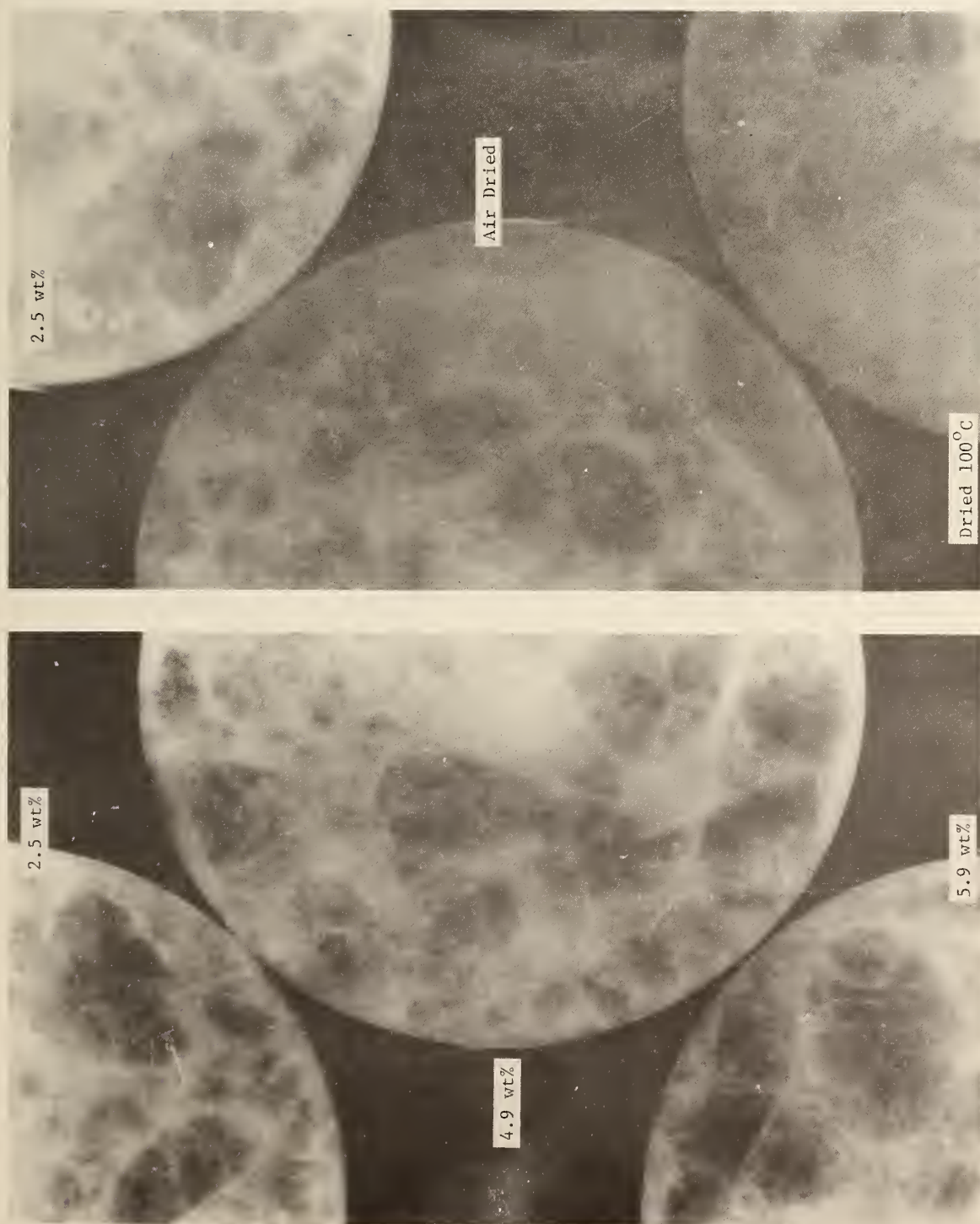
Figure 7-1. Neutron radiograph (negative) of unimpregnated and PMMA-impregnated concrete. Polymer content is indicated. Polymer produces a lighter image. (From Ref. 32.)
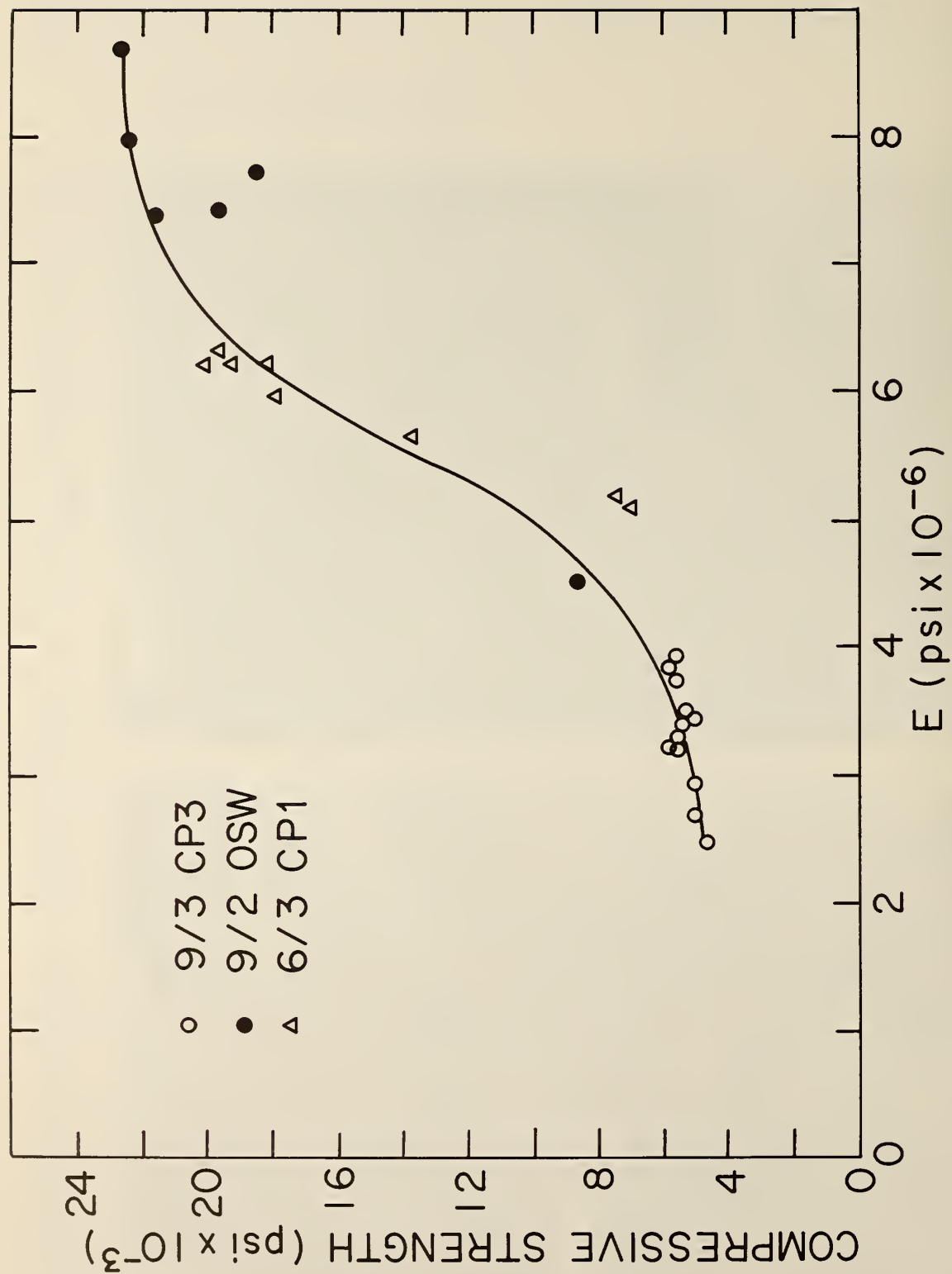
113

Figure 7-2. Elastic modulus and strength for some normal and polymer-impregnated concretes.

5. Resonant Frequency Methods.

ASTM test C 215-60 describes the equipment and procedures for measuring the resonant vibration frequencies of normal concrete beams. The frequency at which a beam resonates is related to the elastic moduli of the beam. From the dimensions, weight, and resonant frequency, the various moduli can be calculated.[55] The procedures described in ASTM C 215-60 were evaluated for use with PIC and worked very well. The increased modulus of PIC was reflected in an increased resonant frequency. The procedure's advantages are similar to those for measuring the elastic modulus: it sees the whole sample, and it is not sensitive to monomer or water. However, the standard instrumentation for this test is not readily adaptable to field work, nor is the technique in general suitable for large samples. Consequently a new instrument for determining the resonant vibration frequencies, based on the acoustic impact principle, was adapted from a commercial source.[56] In the acoustic impact principle the body under test is made to vibrate by continuously striking it with a hammer. The vibration spectrum of the mass is detected with a piezoelectric accelerometer coupled to a sonic analyzer. The testing unit is pictured in Figure 7-3, and a frequency spectrum is shown in Figure 7-4.

The upper limit on the size of sample that can be vibrated has not been determined. However, it appears that signals can be detected through thick walls but, because of the nonideal geometry, would have to be correlated with the modulus. It also appears that signals whose meaning is not completely understood can be obtained by striking and detecting massive concrete from the same surface rather than through the thickness. This implies that the region under impact has been set in vibration. Although this technique holds promise as a simple, rapid, and inexpensive procedure, more work on massive concrete must be done to evaluate it.

6. Schmidt Hammer.

The Schmidt impact hammer is an instrument commonly used in the field for nondestructive testing of concrete. The hammer, basically a sclerometer, measures hardness by impacting a steel rod against the test surface and measuring its rebound. The rebound number is considered indicative of the quality (i.e., strength, durability) of the concrete; the higher the rebound number, the higher the quality. An approximate correlation between rebound number and strength has been observed. For compressive strengths from 3000 to 8000 psi the rebound number varies from about 30 to 50, depending upon the orientation of the hammer.

Initial work with the impact hammer (type N) established that the rebound number varies with polymer loading. This is shown in Figure 7-5 for a series of 3-in.-diam. x 6-in.-long 5000-psi concrete cylinders. Each point is the average of five rebounds, and the results indicate a 65% increase in rebound number for fully
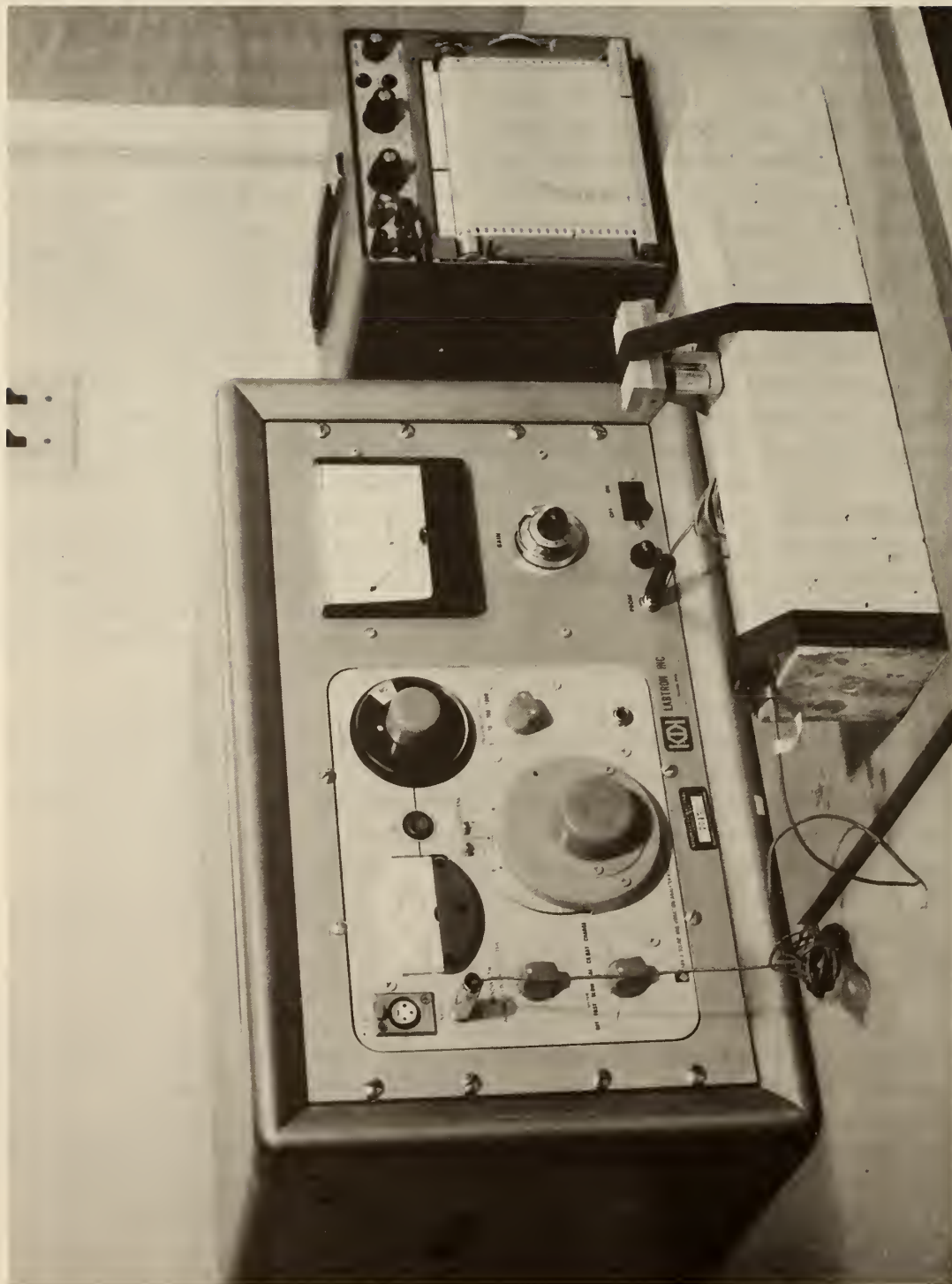
Figure 7-3. Acoustic impact testing unit. A concrete beam is being examined in the transverse mode. The hammer is taped to the center of the beam and the pickup is taped to the end. (From Ref. 36.)
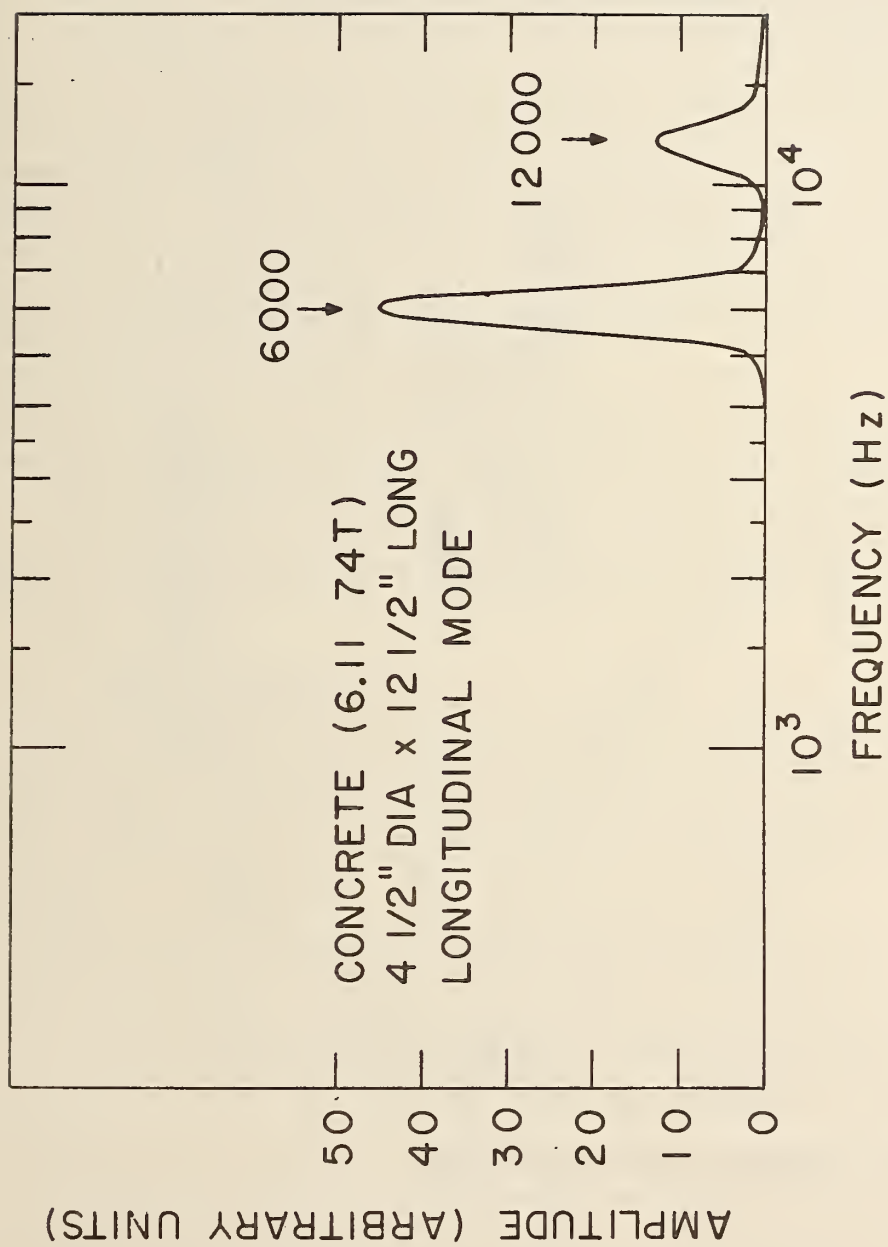
116

Figure 7-4. Longitudinal frequency spectrum of a concrete cylinder showing the fundamental and first overtone. (From Ref. 36.)
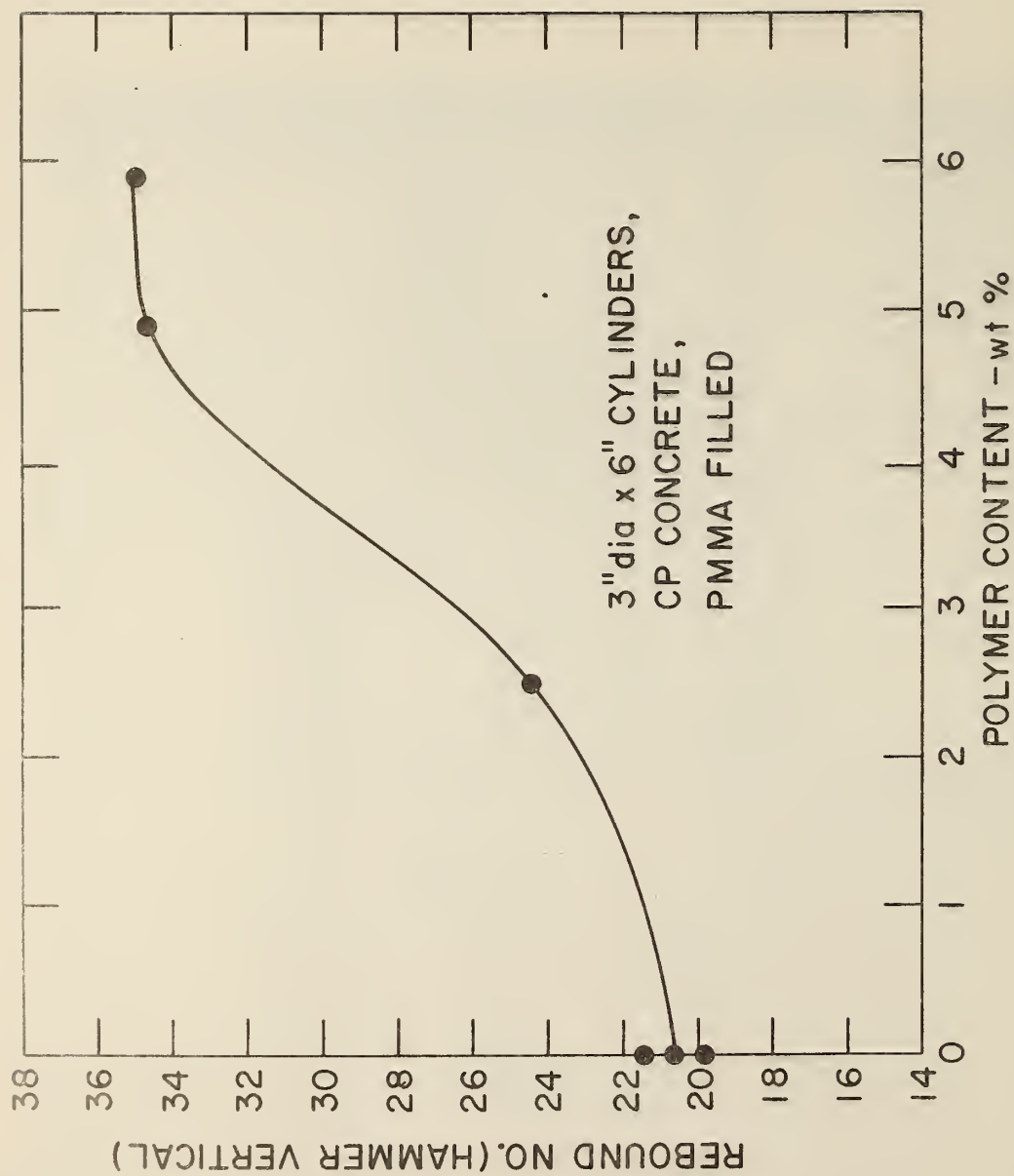
117

Figure 7-5. Schmidt hammer measurements of PMMA-impregnated concrete. (From Ref. 32.)

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impregnated PIC compared with unimpregnated concrete. The
increase is not linear with loading, but is S-shaped, the func-
tion being least sensitive for low- and high-polymer loadings.

A series of 8000-psi 6-in.-diam. x 12-in.-long concrete
cylinders was tested with the hammer. These results are shown
in Table 7-1. Unimpregnated samples had rebound numbers of
about 40, and impregnated samples averaged between 48 and 53.
Here the average increases in rebound number varied from 20 to
33%. An extensive series of Schmidt hammer measurements was
made on 19 pieces of concrete pipe of various sizes. The in-
crease in rebound number with polymer loading varied from 21 to
36% for unreinforced pipe and was independent of wall thickness.
The rebound number increased with increasing wall thickness and
appeared to level off between wall thicknesses of 2 1/2 to 3 in.
(Figure 7-6). This probably indicates the limits of the sensi-
tive range of the Schmidt hammer and suggests that the central
regions of sections with walls more than 5 to 6 in. thick are
inaccessible to the Schmidt hammer.

The Schmidt hammer has certain attractive features for
testing PIC. It is inexpensive, simple, and easy to operate.
The rebound number changes significantly with polymer content,
and is not sensitive to the presence of water or monomer in the
pores. It is best suited for relatively thin sections, since it
appears to have a limited range, which is probably dependent upon
the hammer's size.

7. Sonic Velocity.

Measurement of the velocity of sound waves passing through
concrete has become one of the most powerful and extensively used
non-destructive methods for evaluating the quality of concrete.[55]
Velocity measurements have been used in the field evaluation of
concrete for many years, and an extensive body of literature has
developed.

In general, the higher the sonic velocity, the higher is
the quality of the concrete. Concretes with sonic velocities
>15,000 ft/sec are considered excellent, and those with velocities
<10,000 ft/sec are considered poor. However, sonic velocities
differ greatly according to type of aggregate and dryness of the
concrete.

Since the formation of PIC involves replacing the air or
moisture in the concrete pores with polymer, it was anticipated
that significant increases in the sonic velocity would result.
Consequently measurements were made to investigate the relation-
ship between sonic velocity, polymer loading, and compressive
strength.

Most of the evaluation work was done on 3-in.-diam x 6-in.-
long 5000-psi concrete cylinders. In all cases the sonic velocity

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Table 7-1

Summary of Schmidt Hammer Tests on 6-in.-long x 12-in.-diam.
Cylinders (32)

(3)

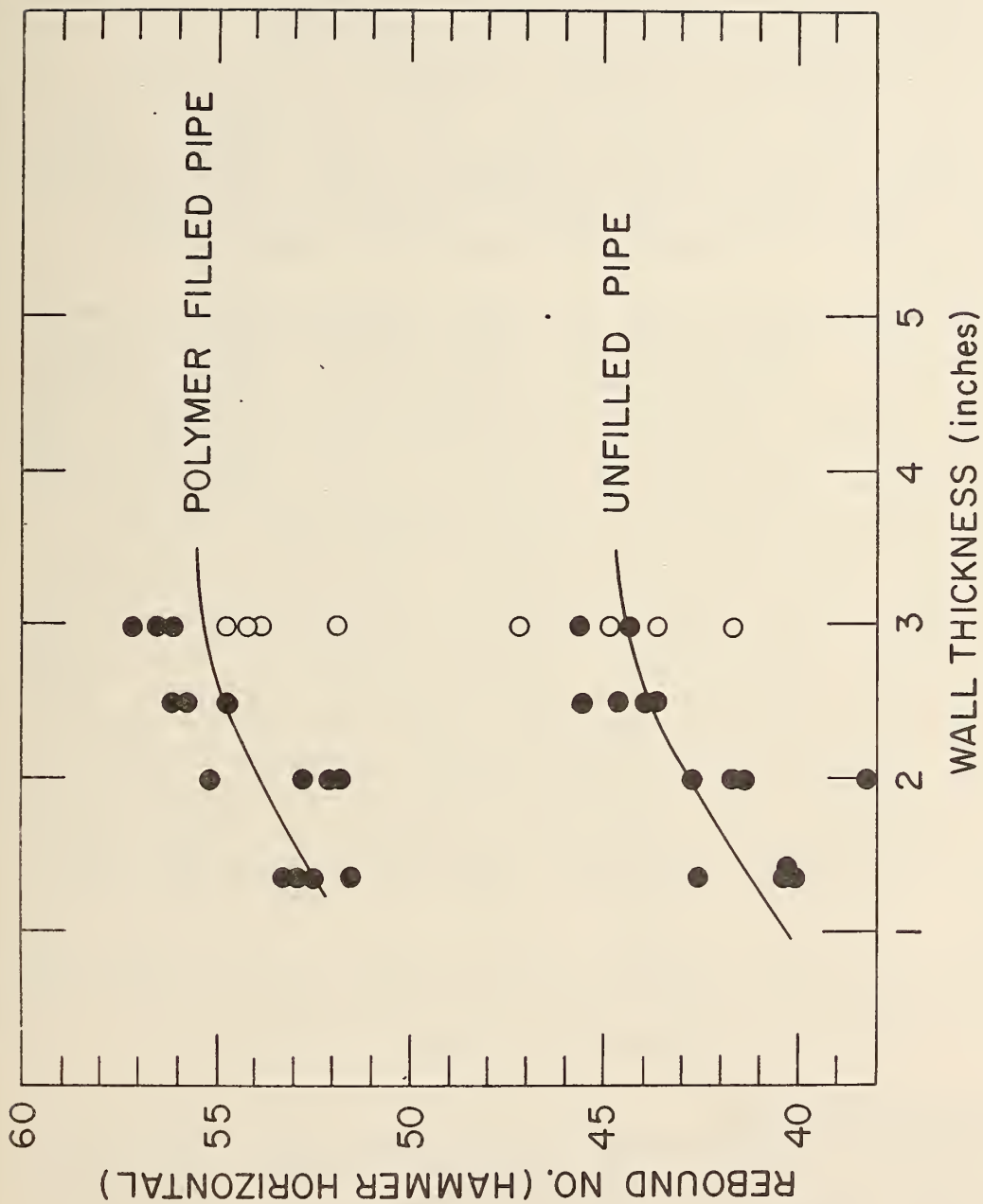| Series	No. of samples	Polymer loading	Rebound No.
OSW-9	9	control	39.8 ± 1.2*
OSW-LA2	2	control	40.6
OSW-8S	18	4.6	53.4 ± 1.8
OSW-8D	17	4.5	53.0 ± 1.3
OSW-9S	9	4.4	51.9 ± 2.3
OSW-9D	9	5.3	48.5 ± 1.1

* Average deviation from the mean.

Figure 7-6. Schmidt hammer tests on polymer-impregnated concrete pipe: rebound number versus wall thickness. Open circles indicate reinforced pipe. (From Ref. 32.)

increased when polymer was present in the concrete. In addition, the velocity of unimpregnated concrete was quite sensitive to moisture content. As shown in Figure 7-7, for between 0 and 1% water content, the velocity can vary by more than 10%. The sonic velocity of the dried sample (dried to constant weight at 125°C) was in the range for poor concrete, and that of the water-saturated concrete was in the range for good concrete. Thus, absolute velocity measurements may be misleading, and for proper comparison of specimens the state of dryness must be specified.

A series of compressive strength specimens was sonically tested before and after polymerization. To permit a range of polymer loadings, half of the specimens were impregnated in the undried condition and half were thoroughly dried. In Figure 7-8 the sonic velocities are plotted against compressive strength. The velocities of the unimpregnated samples are also plotted against strength.

The sonic velocities of the undried, unimpregnated specimens ranged from 11,000 to 12,000 ft/sec. Those of the dried, unimpregnated specimens exhibited considerable scatter, ranging from 7500 to 10,500 ft/sec. On filling the specimens with polymer the sonic velocities of both groups increased to about the same value, about 13,000 ft/sec, although the dried specimens contained about twice as much polymer (≈ 6 wt %) as the undried ones (3 wt %). Thus, the polymer content of the concrete cannot be determined, and neither, therefore, can the strength be estimated, from velocity measurements alone. The results do indicate, however, that the specimens showing the greater change in velocity with polymer loading have higher strengths than those showing a smaller change. In Figure 7-9 the relative velocities, i.e., the ratio of the velocity after impregnation to that before, are plotted against compressive strength. Although there is considerable scatter, a definite trend is apparent. The specimens with the higher velocity ratios have higher strengths. Since these specimens are the ones with the higher polymer content, this trend might have been expected.

One aspect of sonic velocity testing that has not been considered in this work is crack detection. This would be especially promising in evaluating the repair of damaged structures.

8. The Windsor Probe.

The Windsor probe is an impact-type measurement method in which a projectile is fired into a concrete surface under known and reproducible conditions. The pentration depth is considered to be inversely proportional to the strength of the concrete. While no work has been done with the windsor probe on PIC at BNL (some field testing has been done on PC[57]), it is mentioned as another possible technique. It is quite likely that the greater
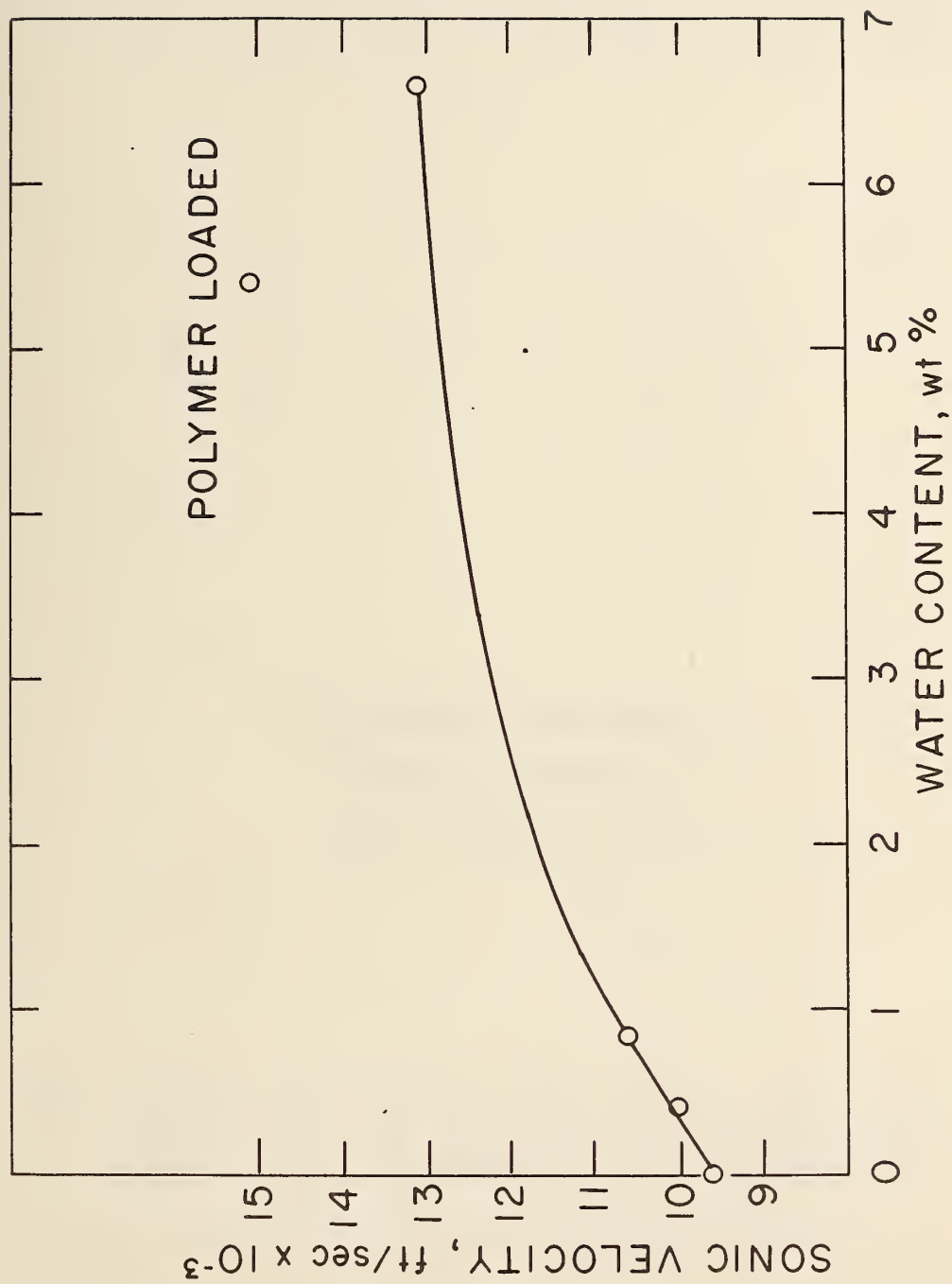
Figure 7-7. Sonic velocity as a function of water content. (From Ref. 31.)
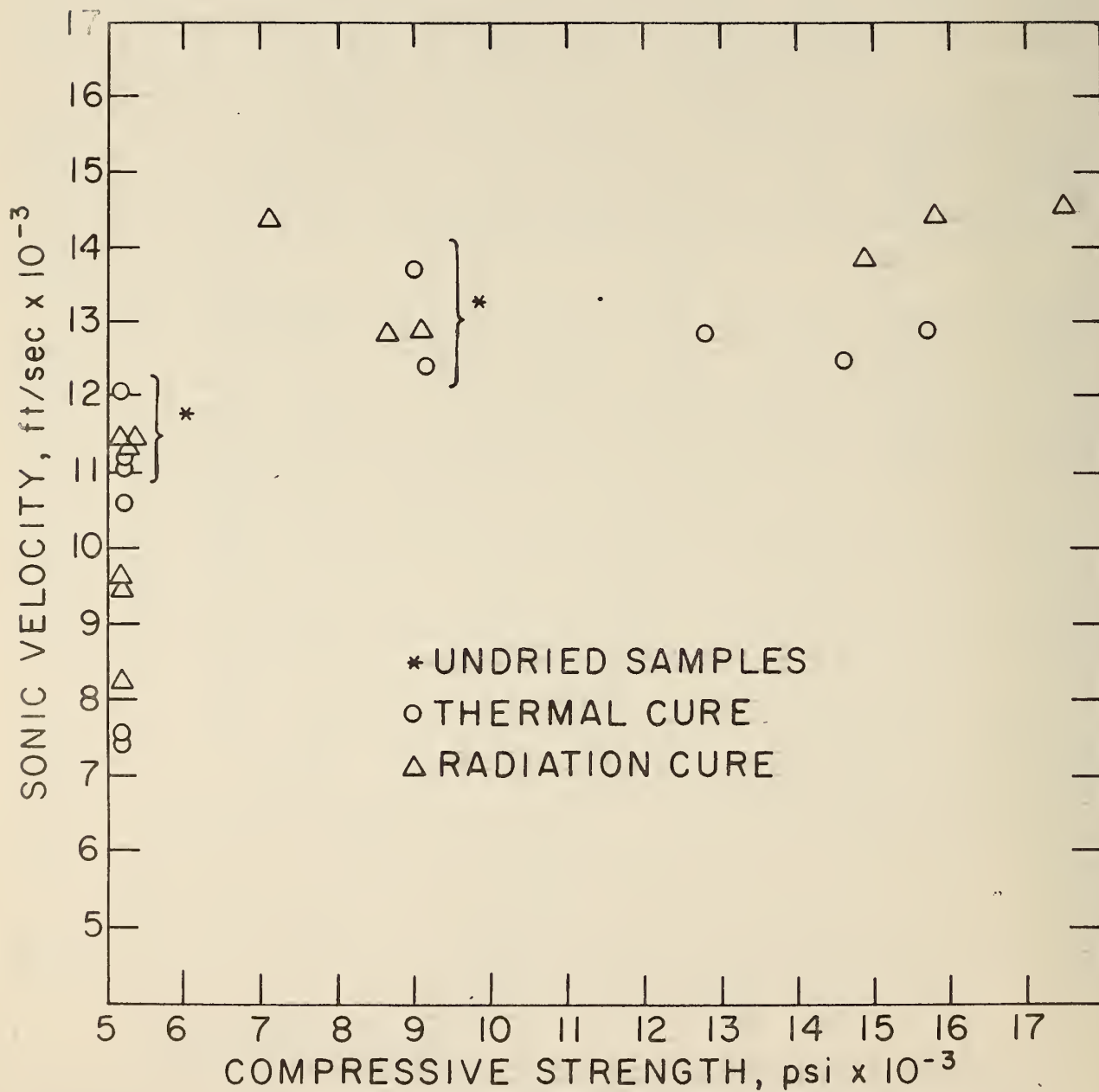
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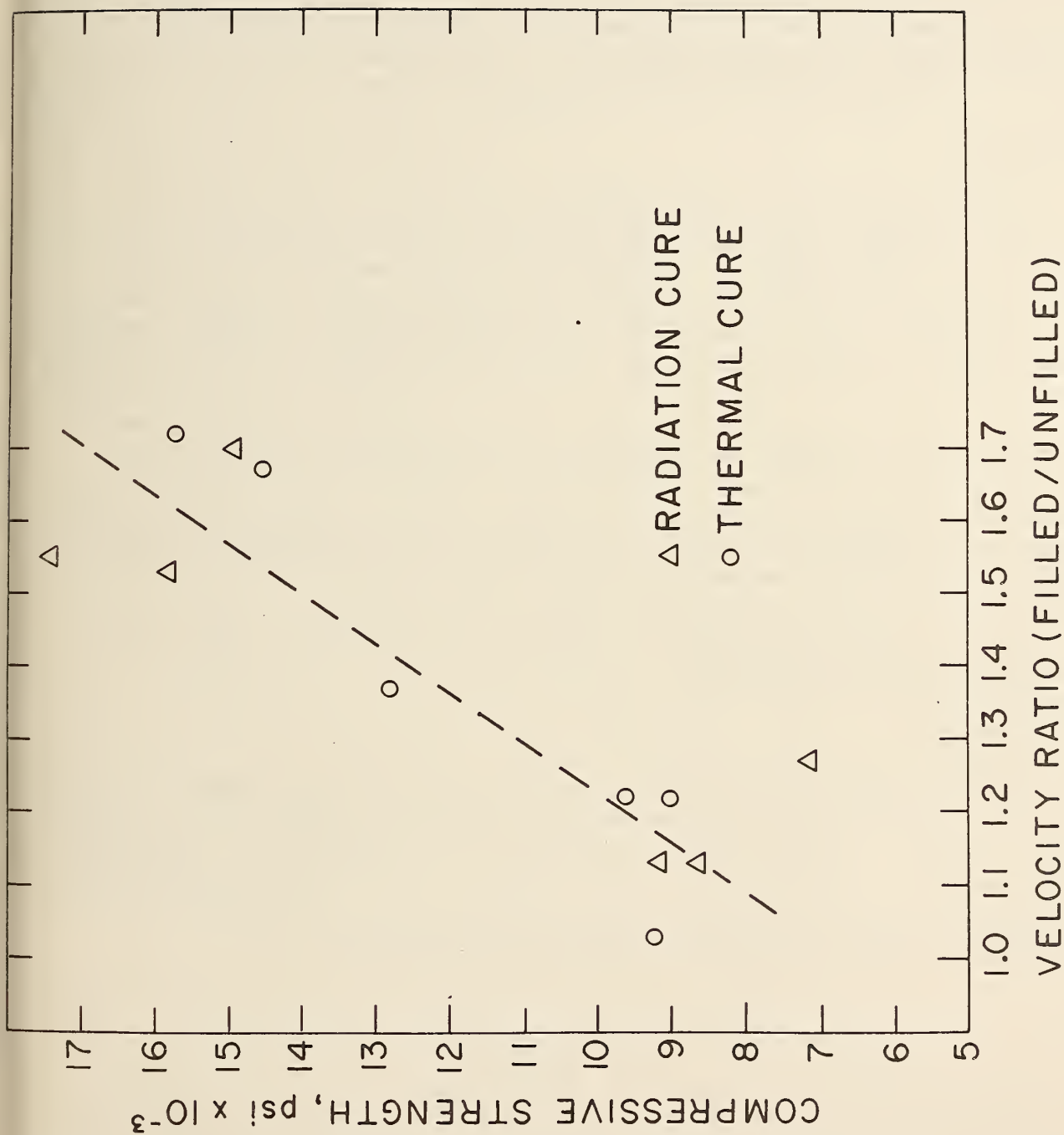Figure 7-8.   Sonic velocity as a function of compressive strength.

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Figure 7-9. Compressive strength as a function of sonic velocity ratio.

strength of PIC, as compared with normal concrete, would be reflected in significantly less penetration of the PIC materials.

9. Coring.

The taking and testing of cores, while not nondestructive in the full meaning of the word, gives results with which it is difficult to argue. It is the standard procedure at BNL for evaluating polymer-treated bridge decks and roads. The procedure is, of course, time consuming, expensive, and requires careful preparation of the samples prior to strength testing.

Discussion

It is obvious that the quality control and nondestructive testing techniques that are applicable to normal concrete are sensitive to the property changes that occur when PIC is formed. However, two important considerations must be kept in mind when PIC is tested: (1) some techniques do not sense the whole sample volume, and (2) some techniques do not discriminate between monomer and polymer.

The recommendation of a particular technique in the present state of the art would be premature. There has been very little application of PIC in the United States. In work on bridge and highway repairs, as mentioned earlier, coring is the procedure of choice. It might be valuable if coring could be combined with one or two of the other techniques described to permit correlation of the various techniques.

For precast applications a number of techniques, with proper controls, would be suitable.

Conclusions

The techniques for quality control and nondestructive testing of polymer-impregnated concrete are available but must be proved in the field. As PIC (and PC) projects are undertaken, consideration should be given to the use of some of the testing methods described here, or others, so that a body of knowledge can be developed from which the best choices may be made.

CHAPTER VIII
FHWA PROGRAMS ON POLYMER-IMPREGNATED CONCRETE
L. E. Kukacka

Introduction

One of the most severe problems facing the highway industry
is the rapid deterioration of concrete bridge decks and other high-
way structures. It has been estimated that more than $70 million
is spent in repairing or replacing deteriorated bridge decks in
the United States each year.

The Offices of Research and Development, Federal Highway Ad-
ministration (FHWA), consider elimination of these problems as one
of their highest priority efforts. The problems and approaches to
their solution are defined in Tasks 4-B-1 and 4-B-2 of the Feder-
ally Coordinated Program of Research and Development under the
titles "Elimination of Spalling and Delamination of Structural
Concrete" and "Development of Materials and Techniques for Rapid
Repair of Deteriorated Concrete." The research described in this
chapter represents work in each of these tasks.

In 1969 the FHWA initiated research at BNL and the USBR on
the use of PIC for highway applications. There are three main
parts to the program: (1) the repair of deteriorated bridge decks
by monomer impregnation, (2) sealing of new bridge decks by partial
impregnation, and (3) the design and structural testing of a system
of prestressed PIC panels for bridge decking.

In addition, several other PIC research programs are in pro-
gress, including a study sponsored by the Texas Highway Department
at the University of Texas on surface impregnation of bridge decks,
work at the California Division of Highways, and a study sponsored
by the National Cooperative Highway Research Program (NCHRP) at
Lehigh University (Study No. 18-2, Use of Polymers in Highway Con-
crete). Descriptions of these programs are given below.

BNL Research

The experimental program at BNL consists of work in three gen-
eral areas: material properties of PIC, repair of deteriorated and
delaminated bridge decks, and partial in-depth impregnation of new
decks. The results of these studies have been published.[17,21,25]

The structural and durability properties of impregnated normal-
weight and structural lightweight concretes have been measured.
The effects of temperature and cyclic loading were investigated and
bond pull-out strength of reinforcement was measured. Process vari-
ables studied include monomer type, method of polymerization, and
air content of the concrete. The results of these tests are summar-
ized in Table 8-1. Compared with the controls, MMA-impregnated

Table 8-1

Summary of Properties of Polymer-Impregnated Concrete

Property	Normal weight concrete								Structural lightweight concrete							
	Air entrained				Non-air entrained				Air entrained				Non-air entrained			
	MMA[a]		S-P[a]		MMA		S-P		MMA		S-P		MMA		S-P	
	P_ℓ[b]	Property[c]	P_ℓ	Property	P_ℓ	Property	P_ℓ	Property	P_ℓ	Property	P_ℓ	Property	P_ℓ	Property	P_ℓ	Property
Compressive strength, psi																
−40°F	7.2	20632	–	–	–	–	–	–	–	–	–	–	–	–	–	–
70°F	7.1	18801	6.6	18578	6.0	18713	5.7	16479	18.9	17671	17.9	17401	16.9	17533	15.5	17739
120°F	7.8	17400	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Tensile splitting strength, psi																
−40°F	7.6	1257	–	–	–	–	–	–	–	–	–	–	–	–	–	–
70°F	7.7	1594	7.4	1314	5.9	1560	5.6	1124	18.5	1923	18.1	1396	16.2	1579	15.7	1419
120°F	7.8	1672	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Flexural strength, psi																
−40°F	8.1	1745	–	–	–	–	–	–	–	–	–	–	–	–	–	–
70°F	8.3	1909	7.5	1138	6.2	1666	5.6	1139	19.9	2229	18.6	1718	16.7	2044	15.9	1609
120°F	8.6	2006	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Freeze-thaw durability cycles/DF[d]; flexural strength[e]	8.1	300/96.2; 1429	7.7	300/74.3; 805	6.1	300/98.2; 1386	5.6	300/79.2; 627	19.4	300/99.1; 2320	18.6	201/40.1; 368	16.9	300/97.5; 1998	15.7	189/37.8; 375
Creep, μ in./in. psi[f]	7.7	0.013	–	–	5.9	0.017	–	–	–	–	–	–	–	–	–	–
Impact energy, ft-lb	7.8	9.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Pullout strength, 10^3 lb																
No. 6 smooth bars	8.1	17.8	–	–	6.1	19.2	–	–	20.3	13.8	–	–	–	–	–	–
No. 6 deformed bars	6.9	33.0	–	–	6.0	29.1	–	–	18.9	36.0	–	–	–	–	–	–
No. 6 smooth bars	5.6	12.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–
No. 6 deformed bars	6.5	33.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Fatigue strength % load/cycles	7.9	70/>10^8	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Coefficient of expansion μ in./in.	7.4	7.1	–	–	5.7	6.5	–	–	–	–	–	–	–	–	–	–
Resistance to scaling[g] control/PIC	7.5	3/0.5	–	–	7.4	3/1	–	–	–	–	–	–	–	–	–	–

a; MMA, methyl methacrylate; S-P, 90 wt% styrene – 10 wt% polyester

b; polymer loading, %

c; average value

d; DF, durability factor

e; flexural strength measurements made after exposure to freezing and thawing

f; 2 mo under load

g; after 109 cycles, rating: 0, no attack; 10, complete disintegration

samples had improvement factors ranging from 2.6 to 4.5. The use of polymer-impregnated concrete as a means of preventing chloride penetration into bridge decks has been demonstrated. This offers a potential solution to the bridge deck deterioration problem.

The feasibility of repairing highly deteriorated and delaminated bridge decks by monomer impregnation has been demonstrated and field testing has been in progress since July 1973. Results to date indicate that highly deteriorated concrete can be reconstituted and bonded to the sound concrete beneath. Compressive and bond strengths of 8000 and 1100 psi, respectively, have been obtained. No deterioration of the repaired sections has been observed after exposure to traffic for 16 months.

During the course of the experimental program, generalized procedures have been developed for drying, monomer impregnation, and polymerization. Descriptions of each of these steps and how they were performed on a highly deteriorated bridge in Greenport, N. Y., are given below.

Drying

Adequate drying of the deck prior to the application of monomer is one of the most important procedures in the impregnation process. Moisture has two deleterious effects. It reduces the amount of porosity in the concrete which is accessible to monomer, thereby reducing the strength and durability, and reduces the bond strength between the polymer and aggregate. An upper limit of 3 wt % has been established for moisture content.

Drying has been accomplished with use of kerosene-fired hot-air heaters (see Figure 8-1). Air heated to 150°C was directed into an asbestos blanket enclosure which was used to box-in the bottom of the deck. Three tests have been performed with the above technique. In the first test, which was severely hampered by rain, a section measuring 10 x 10 ft x 14 in. was dried to a moisture content of 3% in ≈5 days. In two subsequent tests the moisture content of a 6-in. -thick deck was reduced to <0.5% in 4 days (Figure 8-2). Traffic was maintained on the sections during the entire drying operation.

Impregnation

Prior to impregnation the underside of the bridge deck must be sealed to prevent loss of monomer through cracks. This is done by applying a coating of standard polyester resin on underside surfaces showing cracks.

Impregnation is performed with use of a ponding technique. After covering the deck with ≈0.5 in. of dried sand, which serves as a wick and an evaporation barrier, a monomer mixture consisting

Figure 8-1. Air heaters used to dry a bridge deck prior to monomer impregnation.

DRYING DATA
GREENPORT BRIDGE TEST JULY 1974

O, AIR TEMPERATURE WITHIN ENCLOSURE, °C
X, CONCRETE TEMPERATURE 3 IN. FROM BOTTOM °C
△, CONCRETE TEMPERATURE AT TOP SURFACE (6 IN. FROM BOTTOM), °C
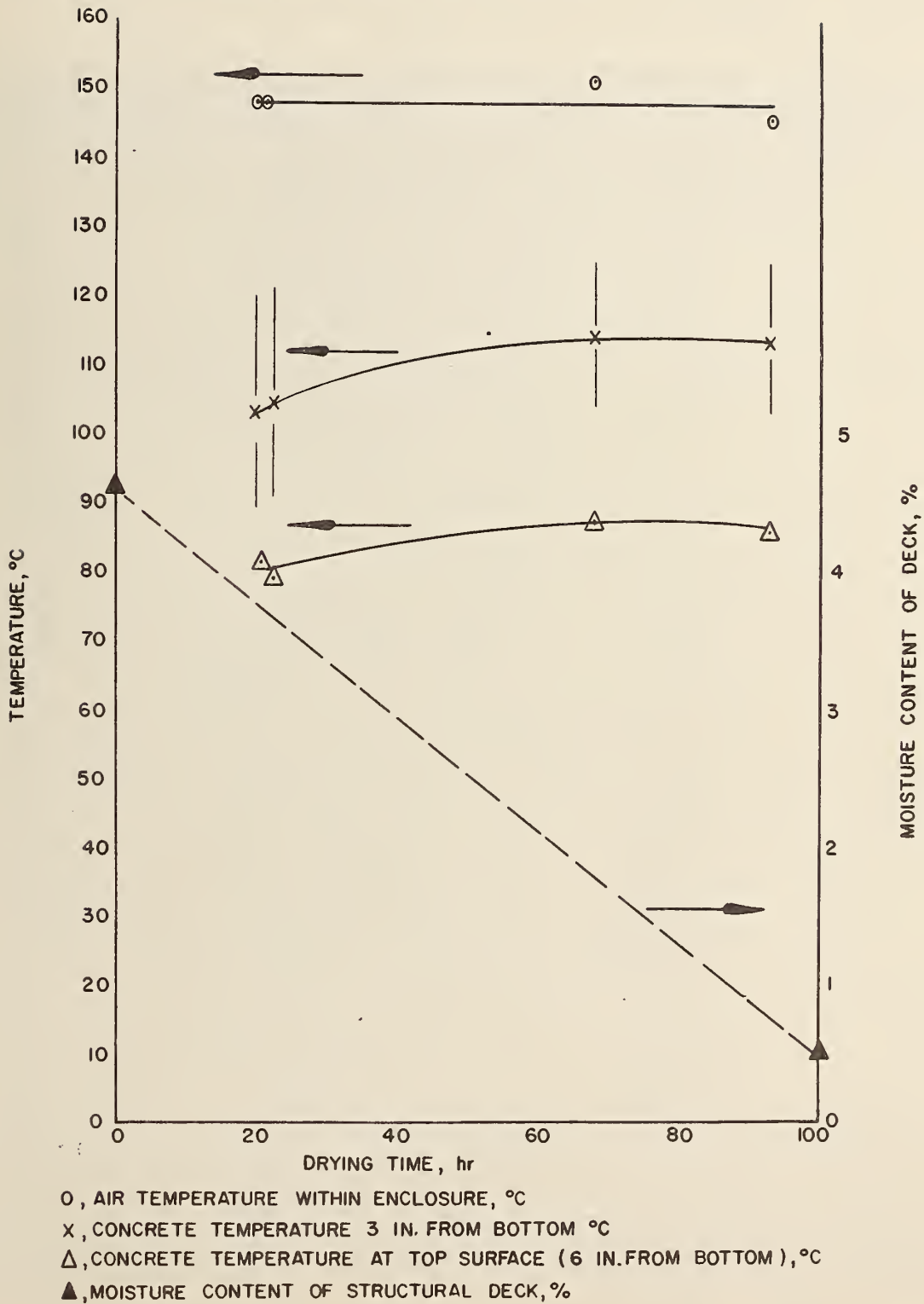▲, MOISTURE CONTENT OF STRUCTURAL DECK, %

Figure 8-2. Temperature profile and moisture content of a bridge deck
during drying.

of 95 wt % methyl methacrylate (MMA) - 5 wt % trimethylolpropane trimethacrylate (TMPTMA) and containing 1% azobisisobutyronitrile (AIBN) catalyst by weight of the monomer, is applied to the sand. Saturation of the sand is continued until the deck is completely impregnated. Soaking for 4 days was sufficient to saturate the 6-in.-thick structural deck at Greenport.

A method for containing the monomer during the soaking period is required. At Greenport this was accomplished by using sections of the concrete wearing course as a dike. If the entire wearing course is removed prior to drying and impregnation, another diking material such as polymer-concrete or a quick-setting cement can be used.

Polymerization

Polymerization of the monomer is easily accomplished by use of the thermal-catalytic technique. The deck is heated to $\approx 70°$C with the hot-air equipment used for the drying operation. Overnight heating is adequate to ensure complete polymerization in a 6-in.-thick deck. After polymerization a polymer-concrete or asphaltic-concrete overlay can be applied to the deck in order to obtain an adequate riding surface.

The procedures described above have been used to successfully treat a 6 x 10-ft section of a highly deteriorated bridge deck at Greenport, N. Y. Because of the high degree of deterioration, cores could not be taken prior to impregnation. Test measurements on cores taken from the impregnated section (see Figure 8-3) indicated compressive strengths and water absorptions of 5000 psi and 1.6%, respectively. These results were confirmed in a subsequent experiment. The New York State Department of Transportation (NYS DOT) is in the process of developing plans for the impregnation of the entire 4000-ft^2 deck. Use of this technique should result in a savings in cost for this project, and in addition the NYS DOT hopes to develop the technique for use as a rapid repair method in areas where high traffic densities make the use of conventional repair methods almost impossible and repair costs prohibitively high.

University of Texas Research

The use of a layer of sand as a monomer reservoir and as a means of reducing evaporation losses during the partial impregnation of bridge decks was developed at the University of Texas.(58)

In the initial work at the University of Texas, simple ponding of MMA resulted in penetration of the concrete to a depth of $\approx 1/4$ in. By placing a thin layer ($\approx 1/4$-in.) of dried fine aggregate over the surface, greater depths of penetration could be achieved

Figure 8-3. Core specimen taken from deteriorated bridge deck after impregnation. Top, polymer concrete. Bottom, impregnated concrete.

(up to 1 in.). The aggregate is reported to act as a wick for the monomer and thus permits longer soak periods (up to 25 hr) without excessive evaporation. It was found that soak times >10 hr produced a substantial polymer surface treatment.

A typical treatment of a field specimen consisted of
(1) covering the specimen with polyethylene to prevent rain from wetting the surface and to dry the slabs;
(2) drying the surface for several days with an electric heating blanket;
(3) removing the heating blanket and covering the slab with $\approx 1/4$ in. of oven-dried lightweight fine aggregate;
(4) applying an initial 2000 to 3000 ml of the monomer system to each 12 ft^2 of surface;
(5) covering the surface with polyethylene to retard evaporation;
(6) shading the surface to prevent a temperature increase, which might initiate polymerization prematurely;
(7) periodically adding additional monomer to keep the sand moist for a minimum soak time of 8 hr; and
(8) applying heat to polymerize the monomer.

Bureau of Reclamation Research

The USBR has developed a field method for the surface impregnation of new bridge decks. Numerous laboratory experiments and two bridge tests have been performed. The following treatment cycle has been used to give 1 to 2-in. penetration depths: (1) surface drying for 3 days at 107° to 121°C, (2) one-day cooling, (3) monomer application and overnight soaking, and (4) polymerization at 60° to 70°C.

Gas-fired heaters rated at 250,000 and 500,000 Btu/hr have been used to dry the concrete to the desired depth of penetration. After cooling, a 3/8-in.-thick layer of sand is spread over the surface. A monomer mixture consisting of 95 wt % MMA – 5 wt % TMPTMA, and containing 0.5 wt % AIBN as the initiator is used to saturate the sand. Polymerization is initiated by heating the deck with use of the gas-fired heaters.

In October 1974 the USBR used the above procedures to treat the surface of a new 28 x 61-ft bridge deck in a suburb of Denver. Penetration depths of up to 1.75 in. were obtained.

California Division of Highways Research

During September 1973, the BNL provided technical assistance to the California Division of Highways for a test in which a

section of the Pit River Bridge, located on Route 5 near Redding, California, was partially impregnated. The experimental effort consisted of impregnating about 2000 ft^2 of the No. 2 northbound lane. Three surface cleaning methods - sand blasting, steam, and bush hammering - were used. Dried and undried sections of each area were impregnated with two monomer systems, 95 wt % MMA - 5 wt % TMPTMA and 60 wt % styrene - 40 wt % TMPTMA. The monomers were applied by using paint rollers and squeegees (see Figure 8-4). In some areas a polyester-TMPTMA coating was applied to the impregnated surface to reduce evaporation losses. Polymerization was initiated by promoter-catalyst techniques. The amount of monomer absorbed was determined on the basis of the quantities applied. Neglecting evaporation losses, values were estimated to range from 0.3 to 1.0 lb/ft^2. The MMA system appeared to penetrate more readily than the styrene-TMPTMA, but variations due to the type of surface treatment were not apparent.

Permeability and petrographic tests were performed on core specimens removed from the treated sections. Compared with the controls, reductions in water permeability of a factor of 10 were obtained. Polymer was found in all specimens, but the depth was highly variable. The maximum depth of penetration was 2 3/4 in. There was no apparent correlation between depth of penetration and the type of monomer or method of surface preparation.

The California Division of Highways is continuing their study of PIC and PC materials.

USBR/Prestressed Concrete Institute Research

In 1972 the Federal Highway Administration (FHWA) initiated a research contract with the Bureau of Reclamation (USBR) for the design and structural testing of a system of prestressed and PIC panels for bridge decking. This study was also strongly supported with funds and engineering services by the USBR and the Prestressed Concrete Institute.

This application for polymer impregnation of concrete was chosen by the FHWA as one possible solution to the problem of bridge deck deterioration. However, in addition to utilizing the resistance of PIC to chemical and freeze-thaw attack, this bridge decking system has the improved strength and other physical properties of PIC.

PIC panels are being evaluated for use as bridge decks. To date, 16-ft-long x 4-ft-wide x 0.5-ft-thick panels prestressed in the longitudinal direction have been impregnated and tested to determine their static and fatigue behavior on a simulated bridge girder configuration. The results of the tests showed that the panels met the design requirements.[10] A preliminary study indicated that this concept of bridge decking may be economical,

Figure 8-4. Application of monomer to a bridge deck in California.

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especially if long-term maintenance costs are considered. Plans
to prepare larger panels for testing on a bridge are being formu-
lated.

CHAPTER IX
FIELD EVALUATION OF POLYMER-CONCRETE
L. E. Kukacka

Introduction

Preliminary field testing of BNL-prepared PC has been in progress for about three years. Initially, several pot holes in a road leading to a receiving depot at BNL were filled with polyester-styrene PC. Since that time, several patches have been made on bridges located at Sag Harbor and Greenport, New York. This work is described in Ref. 25.

On the basis of the results obtained in the preliminary field experiments, PC was used in New York City to repair a badly deteriorated section of a bridge. The work, conducted as a joint venture of the New York State Department of Transportation, the New York City Arterial Highway Maintenance Department, and BNL, involved the filling of a 3 x 10 x 1.25-ft hole through the Third and Lincoln Avenues bridge of the Major Deegan Expressway in the lower Bronx (see Figure 9-1). The high traffic densities in this area ($\approx$85,000 vehicles/day) prevent closing of a lane for >5 hr. Since conventional repair methods could not be used, the hole had been covered with a steel plate.

On December 4, 1973, one lane was closed while the form work was prepared. The hole was filled on December 6 with a PC consisting of 13% monomer (95 wt % MMA - 5 wt % TMPTMA) and 87% of the dense graded aggregate described in Table 9-1. Because the ambient temperature was $\approx$10°C, 2% benzoyl peroxide was used as the catalyst, with a mixture of 2% dimethyl aniline and 1 to 2% dimethyl toluidine as the promoter. A silane coupling agent was added at a concentration of 1.5% to enhance bonding of the adjacent concrete. Mixing and placement were completed in 1 hr with use of conventional equipment. Polymerization was complete within 1 hr, at which time the side forms were removed. The completed patch is shown in Figure 9-2. At an age of 1 hr, estimates of the compressive strength made with use of a Windsor probe indicated values ranging between 5400 and 8000 psi. The measured compressive strength of a cylinder cast from the same mix was 12,200 psi, and the water absorption was 0.4%. At 3:00 p.m., 5 hr after starting work and 2 hr after completion of the placement, the lane was reopened to traffic. The top and underside of the section have been inspected on a routine basis. After 7 months in service, no changes have been noted. Work to repair five larger holes in the bridge is scheduled.

Cost Estimates for Polymer-Concrete

Because the number of small-scale field tests performed to

Figure 9-1. Hole in bridge on Major Deegan Expressway prior to filling with polymer-concrete.

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Table 9-1

Sieve Analysis for Aggregate Used in Polymer Concrete

Sieve size	Quantity passing through sieve, %
3/4 in.	94.8
1/2 in.	83.1
3/8 in.	78.1
1/4 in.	61.6
No. 4	51.8
No. 8	40.9
No. 16	37.1
No. 30	30.5
No. 50	11.0
No. 100	2.6
No. 200	1.2

Figure 9-2. Completed polymer-concrete patch in bridge on Major Deegan Expressway.

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date is small, only the material costs associated with the use of PC have been determined. Attempts to determine placement and traffic control costs will be made in conjunction with future repair work on the Major Deegan Expressway.

Since the required formwork and the placement techniques for PC are basically the same as those used for portland cement concrete, the installation costs should be similar. Traffic control costs will be significantly lower because of the shorter cure time. Future maintenance costs should also be reduced.

The cost for the materials used in the first test on the Major Deegan Expressway was $302/yd^3. Of this total, $77 was directly attributable to the low ambient temperature (10°C) during placement which necessitated the use of 1.25 wt % dimethyl toluidine (cost, $9.50/lb) in conjunction with 2 wt % dimethyl aniline ($1.50/lb) as the promoter and 2 wt % benzoyl peroxide ($1.26/lb) as the catalyst. For temperatures $>20^{\circ}$C, 1 wt % benzoyl peroxide and 1 wt % dimethyl aniline would be sufficient to product complete polymerization in <60 min.

Further reductions in cost can be obtained by using polyester-styrene. PC containing 10 wt % of a 54 wt % polyester – 46 wt % styrene mixture produces compressive strengths of $\approx$10,000 psi in <60 min. Polymerization conditions for the mixture were given in Chapter V. Based on a current price of 37¢/lb for the polyester-styrene, the materials for this mix can be obtained for $170/yd^3.

Compared with portland cement concrete, PC is expensive and as a result it will probably not be used as a general substitute for concrete. There are, however, many specific applications where the properties of concrete are inadequate. One such application would appear to be as a specialized bridge deck or pavement patching material. For these applications, PC's high strength, rapid curing characteristics, and good durability will result in minimum traffic delays, improved safety, and in some cases may eliminate the necessity of constructing expensive detours. In these cases, the material cost becomes insignificant.

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MONOMER POLYMERIZATION CONDITIONS

1. 95 wt % MMA - 5 wt % TMPTMA
    24°C   ambient temperature
    1.5%   benzoyl peroxide
    1%   DMA (dimethyl aniline)
    1/2%   DMT (dimethyl-p-toluidine)
    Gel time in PC, ≈25 to 30 min
    Cure time of PC, ≈45 to 60 min

    If ambient temperature goes up to 32 to 35°C, the gel time will decrease by about 5 to 10 min. If increased working time is needed, cut catalyst-promoter concentrations by 1/4 to 1/2%.

    If ambient temperature goes down to 7 to 13°C, increase the catalyst and promoter concentrations by 1/4 to 1/2%.

2. 50 wt % polyester - 50 wt % styrene
    24°C   ambient temperature
    1%   methyl ethyl ketone peroxide
    1/2%   cobalt naphthenate
    Gel time in PC, ≈20 to 30 min
    Cure time in PC, ≈40 to 50 min

    If ambient temperature rises to 32 to 35°C, reduce catalyst and promoter concentration by 1/4%.

    If ambient temperature goes down to 7 to 13°C, addition of 1/4% DMA will keep the gel time at ≈20 to 25 min and cure time at ≈40 min.

3. 75 wt % styrene - 25 wt % polyester
    24°C   ambient temperature
    1%   methyl ethyl ketone peroxide
    3/4%   cobalt naphthenate
    Gel time in PC, ≈25 to 30 min
    Cure time in PC, ≈40 to 50 min

    If ambient temperature rises to 32 to 35°C, reduce the catalyst and promoter concentration by 1/4% to retain ≈20 to 25 min gel time.

Note:

   The composition of most polyesters used at Brookhaven National Laboratory is 65 wt % polyester - 35 wt % styrene as received from the manufacturer. To make a 50 wt % polyester - 50 wt % styrene mixture, add 30 wt % styrene to the manufacturer's 65 wt % polyester - 35 wt % styrene mixture.

APPENDIX B

SUPPLIERS OF MATERIALS FOR CONCRETE-POLYMER COMPOSITES

	Cost/lb, as of July 1974	
	55-gal drum (440 lb)	Tank car (40,000 lb)
Methyl Methacrylate	$0.38	$0.31

Rohm and Haas Co.
465 Boulevard
East Patterson, N. J.

E.I. du Pont de Nemours & Co.
Wilmington, Del.

Union Carbide Corp.
Chemicals and Plastics
New York, N. Y.

Styrene	$0.40	$0.30

Dow Chemical Co.
Park 80 Plaza East
Saddle Brook, N. J.

Union Carbide Corp.
Chemicals and Plastics
New York, N. Y.

Monsanto Chemical Co.
800 N. Lindbergh, Blvd.
St. Louis, Mo.

Koppers Co., Inc.
Koppers Building
Chemical and Dyestuffs Division
Pittsburgh, Pa.

Shell Chemical Corp.
Industrial Chemicals Division
110 West 51st Street
New York, N. Y.

Polyester-Styrene	$0.45	$0.40

W. R. Grace and Co.
Marco Chemical Division
1711 Elizabeth Avenue
West Linden, N. J.

Cost/lb

Diamond Shamrock Chemical Co.
Plastics Division
Cleveland, Ohio

Arco Chemical Co.
Philadelphia, Pa.

Reichhold Chemicals, Inc.
White Plains, N. Y.

Rohm and Haas Co.
East Patterson, N. J.

Durez
Division of Hooker Chemical Corp.
North Tonawanda, N. Y.

Cross-Linking Agent
Trimethylolpropane Trimethacrylate (TMPTMA)

$2.00

Rohm and Haas Co.
465 Boulevard
East Patterson, N. J.

Sartomer Co., Inc.
Division of Sartomer Industries, Inc.
Bolmar and Neilds Streets
West Chester, Pa.

Catalysts

1.	Benzoyl peroxide	$1.20
2.	Methyl ethyl ketone peroxide	$2.10
3.	Luozo A79	$5.25
4.	Azobisisobutyronitrile (AIBN)	$18.00

Lucidol Division (1,2,3)
Pennwalt Corp.
1740 Military Road
Buffalo, N. Y.

Reichhold Chemicals Inc. (1,2)
White Plains, N. Y.

Cost/lb

Shell Chemicals Inc. (1,2)
Houston, Texas

Polysciences Inc. (4)
Warrington, Pa.

E.I. du Pont de Nemours & Co. (4)
Wilmington, Del.

Promoters (Accelerators)

1.	Dimethyl Aniline	$ 3.00
2.	Dimethyl Toluidene	$16.50
3.	Cobalt Naphthenate	$ 1.30

Berton Plastics Co. (3)
170 Wesley Street
So. Hackensack, N. J.

Polysciences, Inc. (1,2)
Warrington, Pa.

Silane Coupling Agents $ 1.25

Union Carbide Corp.
Chemicals and Plastics
New York, N. Y.

Dow Corning Corp.
Midland, Mich.

Inhibitors

1.	Hydroquinone	$ 2.00
2.	Methyl-ethyl-hydroquinone	$ 2.25
3.	Tert.-butyl-catechol	$ 1.75

Diamond Shamrock Chemical Co. (1)
Chemicals Division
711 Pittman Road
Baltimore, Md.

Eastman Chemical Products Inc. (1,2)
Subsidiary of Eastman Kodak Co.
P. O. Box 431
Kingsport, Tenn.

Cost/lb

Mallinchrodt Chemical Works (1)
P. O. Box 5439
St. Louis, Mo.

Dow Chemical Co. (3)
Midland, Mich.

Solvents

1. Acetone $0.15
2. Trichloroethane $0.20

Ashland Chemical Co. (1,2)
Industrial Chemicals and
Solvents Div.
Columbus, Ohio

J. T. Baker Chemical Co. (1)
Phillipsburg, N. J.

Mallinchrodt Chemical Works (1)
St. Louis, Mo.

Monsanto Chemical Co. (1)
St. Louis, Mo.

Diamond Shamrock Chemical Co. (2)
Cleveland, Ohio

Hooker Chemical Co. (2)
Industrial Chemicals Division
Niagara Falls, N. Y.

FHWA

R&D